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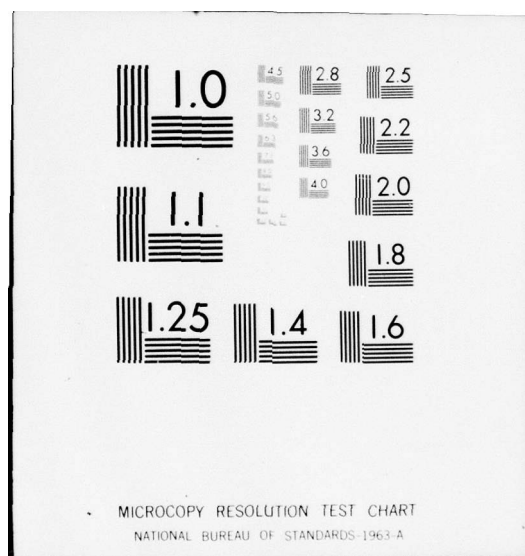
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CONTRACT NO. N00019-76-C-0138

**"QUALITY CONTROL OF STRUCTURAL
NONMETALLICS"**

McDonnell Aircraft Company
McDonnell Douglas Corporation
St. Louis, Missouri

June 1977

Final Report for Period 15 October 1975 - 14 October 1976

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Nonmetallic materials are now being used in primary structural applications, principally as advanced composites and adhesives. These resin systems are initially subjected to several years of extensive qualification testing ranging from coupon testing to the destructive testing of large substructures to establish a statistical base for design analysis and to establish environmental durability.

The processability, strength and durability of any material must ultimately depend on their physical and chemical characteristics. However, most state-of-the-art adhesive and composite prepreg resin systems are proprietary in nature and are not identified as to their chemical composition. The user must rely almost entirely on performance tests such as short-term mechanical testing, flow times, etc., as a means of batch-to-batch quality control. While these performance type quality control tests have served acceptably during the introduction of these materials, the user must move toward additional quality assurance test capabilities to insure chemical consistency to that formulation which was initially qualified.

During this program, chemical characterization test methods applicable to structural epoxy resin systems have been developed and the viability of these techniques for in-plant quality control and the establishment of acceptance criteria with statistically valid accept/reject limits have been demonstrated.

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FOREWORD

The following final report describes work performed on NASC Contract No. N00019-76-C-0138, "Quality Control of Structural Nonmetallics". The work accomplished and reported herein was performed by the McDonnell Aircraft Company, McDonnell Douglas Corporation, St. Louis, Missouri. The program was administered under the direction of Naval Air Systems Command by John Gurtowski.

The program was conducted by the Material and Process Development Department at McDonnell Aircraft Company, St. Louis, and was managed by R. J. Juergens, with J. F. Carpenter as Principal Investigator. Major contributors to the program include T. T. Bartels, J. B. Maynard, W. A. Mathew, and C. E. Wilson of the Materials Laboratory.

Data reported herein was generated in the laboratories of McDonnell Aircraft, St. Louis, and was not supplied by the vendors of the materials investigated unless specifically so stated in the text of the report.

This report covers the contract period 15 October 1975 to 14 October 1976.

This technical report has been reviewed.

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1. INTRODUCTION

High performance military aircraft are using nonmetallic materials in primary structural applications, principally as advanced composites and adhesives. These resin systems are initially subjected to several years of extensive qualification testing ranging from coupon testing to the destructive testing of large substructures to establish a statistical base for design analysis and to establish environmental durability. Manufacturing procedures must be developed and standardized. These expenditures together with the liabilities associated with the integrity of any structure whose failure can result in the loss of an aircraft represents an investment of hundreds of thousands to tens of millions of dollars.

The processability, strength and durability of any material must ultimately depend on their physical and chemical characteristics. However, most state-of-the-art adhesive and composite prepreg resin systems are proprietary in nature and are not identified as to their chemical composition. The user must rely almost entirely on performance tests such as short-term mechanical testing, flow times, etc., as a means of batch-to-batch quality control.

While these performance type quality control tests have served acceptably during the introduction of these materials, the user must move toward additional quality assurance test capabilities to insure chemical consistency to that formulation which was initially qualified.

It has been the objective of this program to develop analytical test methods applicable to structural epoxy resin systems and demonstrate the viability of these techniques for in-plant quality control and the establishment of acceptance criteria with statistically valid accept/reject limits.

2. SUMMARY

The program was divided into three phases of investigation. The objectives as well as a summary of the results for each phase are described below:

Phase I - The major objective of the phase was to select candidate materials and test methods for subsequent phases of the program. The materials selected were:

- (1) Narmco T300/5208 Graphite/Epoxy Prepreg
- (2) Hercules AS/3501-6 Graphite/Epoxy Prepreg
- (3) American Cyanamid FM400 Adhesive
- (4) American Cyanamid BR400 Primer

Vendors for the candidate materials were contacted to assure their cooperation in supplying the appropriate special test batches of materials having known controlled variation in formulation and processing parameters. Arrangements were also made for obtaining a number of different batches of material representing the vendor's standard production.

Based on the material selection, preliminary test methods were selected for chemical separation, quantitative analysis and physiochemical quality control tests. The techniques initially selected included: gel permeation chromatography, liquid-liquid chromatography, gas-liquid chromatography, atomic absorption and infrared analysis. Other techniques of physiochemical control investigated were thermal analytical techniques and dynamic dielectric analysis.

Phase II - The objective of this phase was to chemically analyze the selected resin systems and to develop methods and perform testing necessary to establish practical quality control tests and acceptance criteria based on the chemical formulation of each of the systems. This objective was accomplished for each resin according to the following sequential tasks:

- o Separation and identification of the components
- o Quantitative determination of weight percent for each component
- o Thermal characterization
- o Selection, development and adaption of methods suitable for receiving quality control
- o Use of the quality control methods for replicate testing of a representative number of production batches of vendor qualified material

- o Testing of special batches of material that were prepared by the vendor to have controlled variations in chemical formulation.

Phase III - The objective of this phase was to establish chemical acceptance criteria for each resin. The effort included:

- o Documentation of the test methods and results.
- o Data reduction to establish statistically valid acceptance criteria

3. TECHNICAL APPROACH AND ORGANIZATION OF DATA

3.1 Technical Approach

The general technical approach used to accomplish the goals of this program is outlined in Figure 1.

Initially, each of the resin systems was separated and the individual constituents quantitatively determined. This information was used as the basis for selection and development of practical test methods suitable for receiving quality control for chemical formulation and thermal characterization of each batch. It is not necessary, and would be costly, to perform a complete quantitative analysis as a part of the receiving inspection for each batch.

The selected quality control methods were used for replicate testing of four or five batches representing the vendors' standard production material. These data were statistically reduced to provide an "A" allowable spread to establish accept/reject limits.

Special batches with known variations in chemistry were supplied by the vendors. These intentionally "off-specification" batches were tested to help establish the applicability, sensitivity, and accuracy of the test methods.

Thermal analysis by differential scanning calorimetry (DSC) was found to be a useful quality control tool. A change in degree of resin advancement, or B-staging, can be detected as well as certain variations in chemical formulation for the prepreg resins.

Dynamic dielectric analysis was investigated and later abandoned as a routine quality control tool of practical importance to the particular resin systems investigated in this program.

3.2 Organization of Data

To afford continuity and ease of reference, each of the resins are reported on an individual basis in the subsequent sections of this report with detailed test procedures given in the Appendix. The data for each resin system is organized according to the following subsection sequence:

- (1) Resin Analysis
- (2) Identification and Quantitative Determination of Resin Components
- (3) Thermal Analysis and Characterization
- (4) Testing of Production Batches
- (5) Testing of Special Batches with Known Chemical Variations
- (6) Recommended Quality Control Tests and Acceptance Criteria

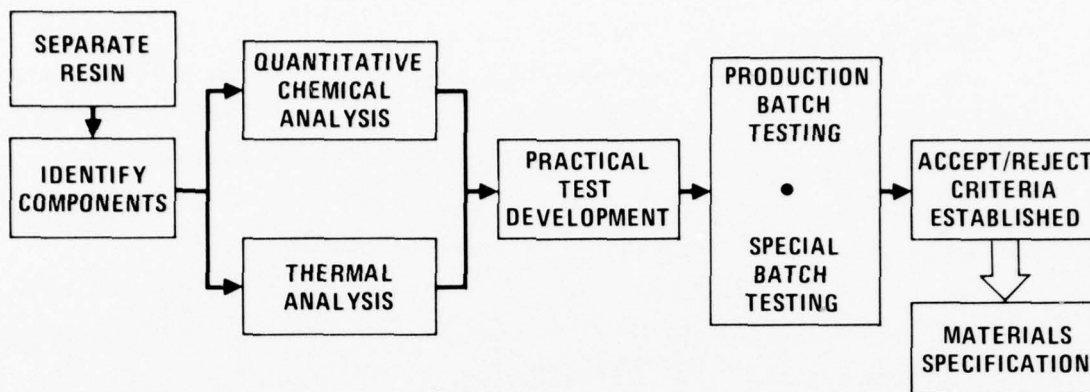


FIGURE 1
TECHNICAL APPROACH FOR ESTABLISHING PHYSIOCHEMICAL
QUALITY CONTROLS FOR ADHESIVES AND PREPREGS

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3.3 Coding of Data

For the purpose of this report, certain of the resin components are identified by code designations, such as Epoxide No. 1, No. 2, etc., rather than by their trade or chemical names. Coding is consistent for each individual resin formulation; however, epoxide designations are not necessarily the same between formulations, e.g., Epoxide No.2N for the 5208 resin is not the same as Epoxide No.2H for the 3501-6 resin.

4. NARMCO T300/5208 GRAPHITE/EPOXY PREPREG

4.1 Resin Analysis for 5208

The quantitative analysis of 5208 resin is given in Table 1.

TABLE 1

ANALYSIS OF 5208 RESIN

<u>Component</u>	<u>Analysis Parts/100 Resin (phr)</u>	<u>Percent (Wt.)</u>
Epoxide No. 1N	100	67.6
CIBA Eporal (Curing Agent)	34	23.0
Epoxide No. 2N	14	9.5

Results in Table 1 are reported in parts per hundred resin (phr) by weight, as well as weight percent. Resin formulators prefer to work with phr, and the nearest whole number for phr is normally used.

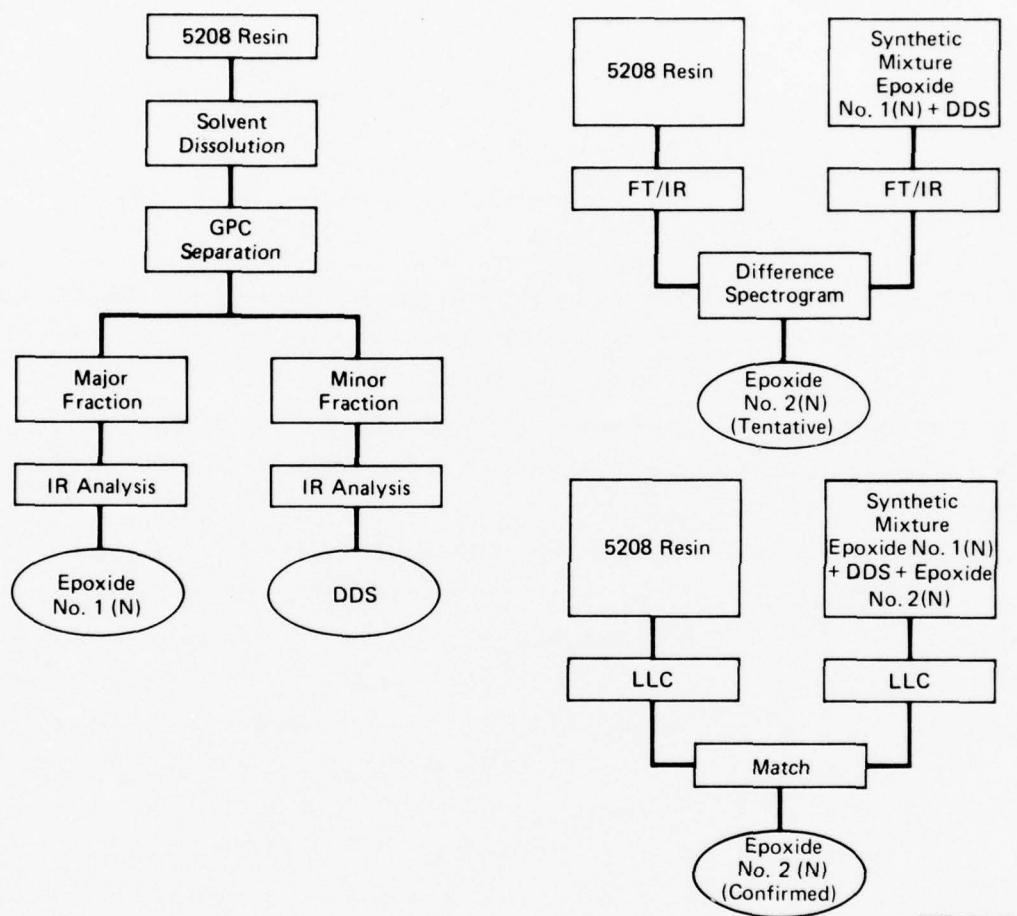
4.2 Identification and Quantitative Determination of 5208 Components

The schematic for 5208 resin separation and component identification is shown in Figure 2.

The two major components, Epoxide No. 1N and CIBA Eporal (DDS), were identified by infrared analysis of the fractions obtained using gel permeation chromatography (GPC). Figure 3 shows the GPC separation of the components on the basis of molecular size. The infrared spectra of the GPC fractions were compared with the spectra for individual samples of Epoxide No. 1N and DDS, Figures 4 and 5.

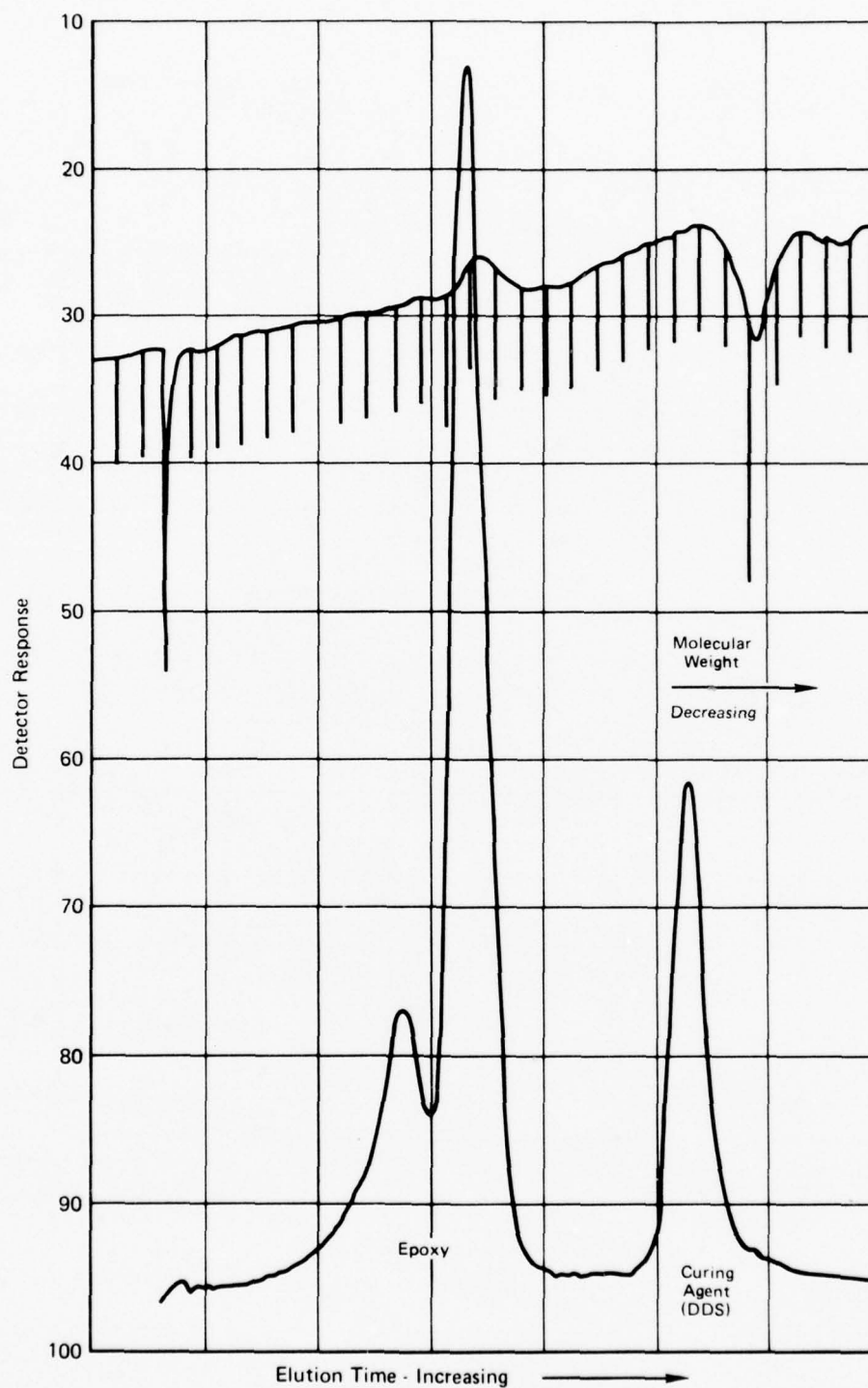
Work being carried out at the Naval Research Laboratory using nuclear magnetic resonance (NMR), Reference (1), and Lockheed Missiles and Space Corporation using infrared and thin layer chromatography (TLC), Reference (2), suggested that 5208 contained a third component which was tentatively identified as Epoxide No. 2N. We compared the spectra obtained by fourier transform infrared (FT/IR) analysis for 5208 with a synthetic mixture containing Epoxide No. 1N and DDS. The difference spectra obtained by subtraction of the digitized and normalized spectra showed the major absorbance bands for Epoxide No. 2N, Figure 6. Finally, conclusive evidence that Epoxide No. 2N was a component of the 5208 system was obtained by reverse phase liquid-liquid chromatography (LLC) using a 30/70 volume percent tetrahydrofuran/water elution-solvent system.

The sulfone curing agent (DDS) was determined to be 23% by weight, using the quantitative IR method given in the Appendix. The DDS, in chloroform



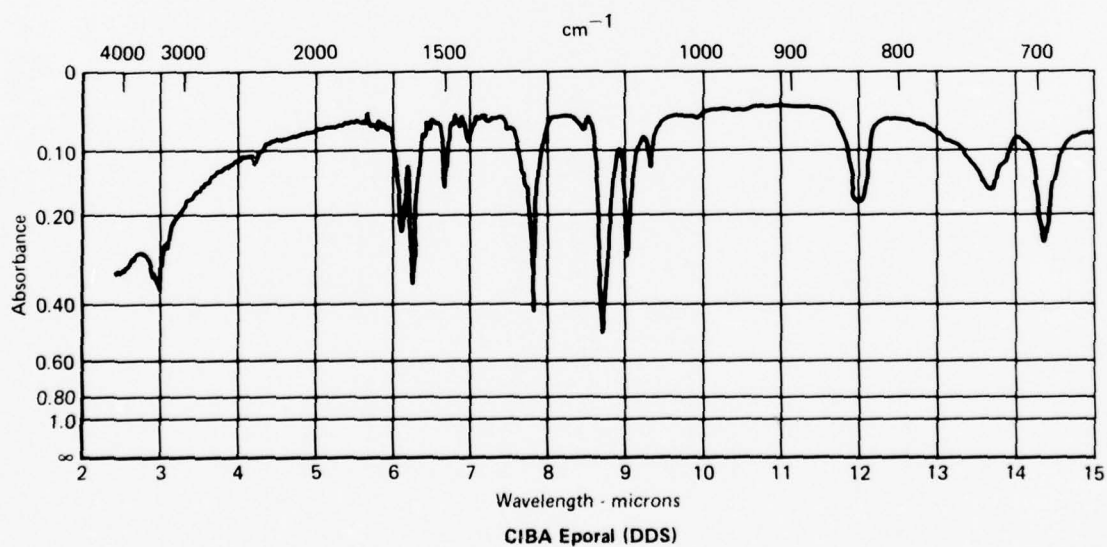
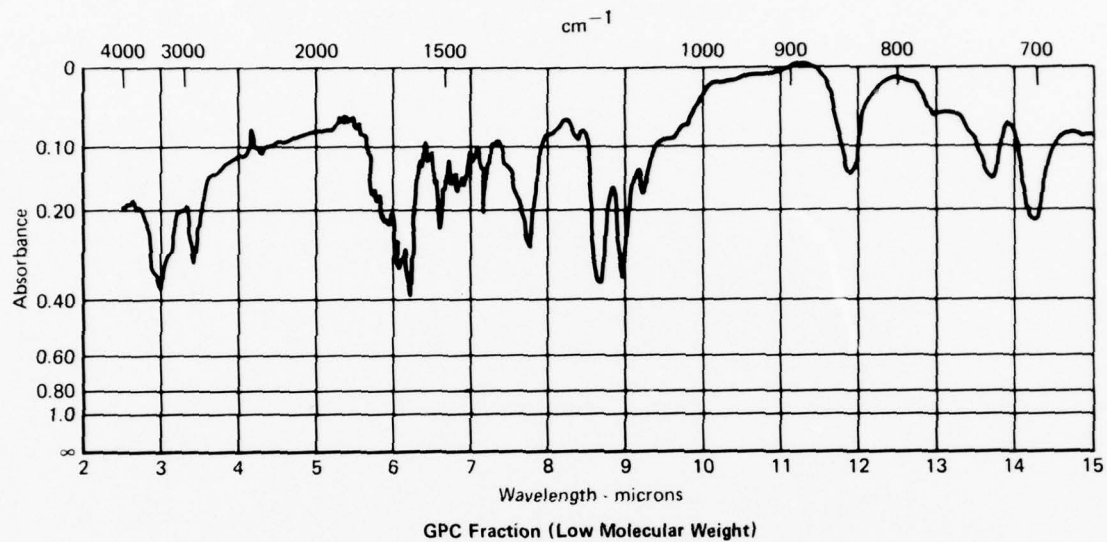
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FIGURE 2
SEPARATION AND IDENTIFICATION OF 5208 RESIN COMPONENTS



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FIGURE 3
SEPARATION OF NARMCO 5208 RESIN BY GEL PERMEATION CHROMATOGRAPHY



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FIGURE 4
IR IDENTIFICATION OF SECOND GPC
FRACTION FOR NARMCO 5208

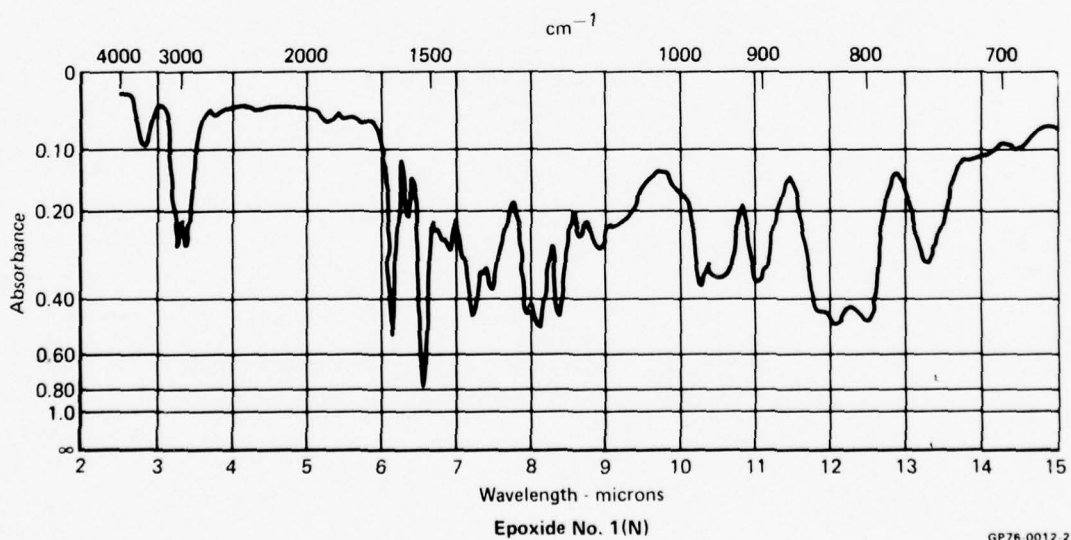
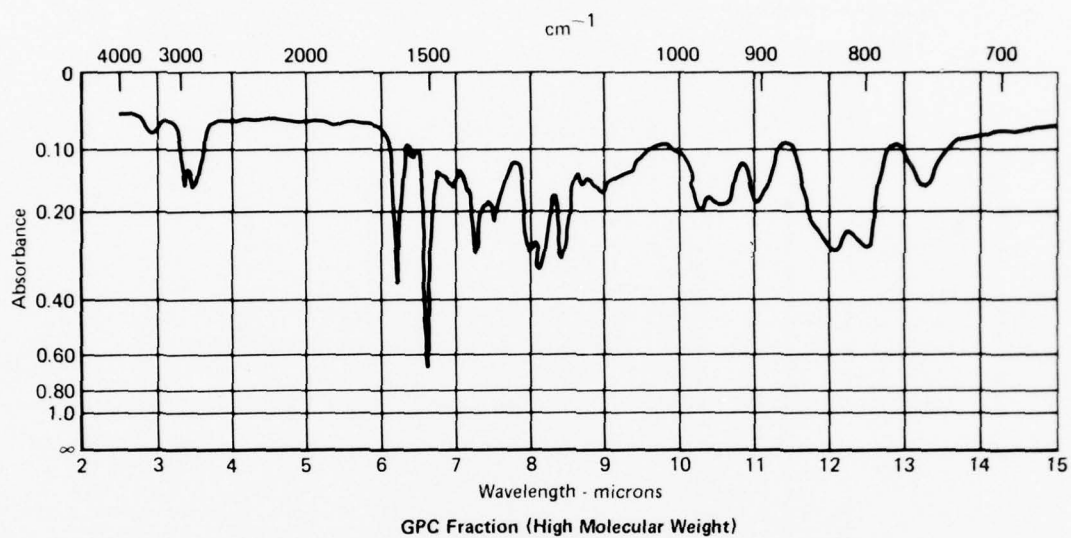
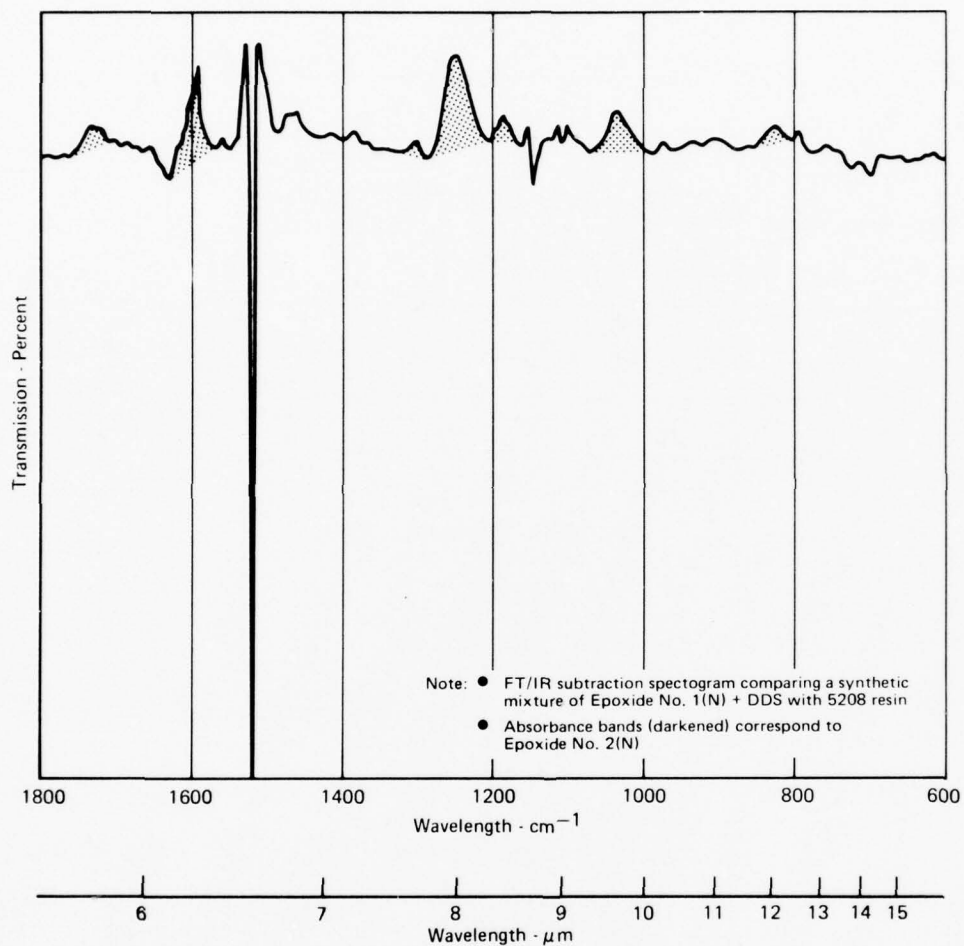


FIGURE 5
IR IDENTIFICATION OF FIRST GPC
FRACTION FOR NARMCO 5208

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FIGURE 6
IDENTIFICATION OF MINOR EPOXY COMPONENT IN 5208 RESIN
BY FOURIER TRANSFORM INFRARED (SUBTRACTION METHOD)

solution, exhibits a strong interference-free absorbance band at 1110 cm^{-1} suitable for quantitative measurements.

The Epoxide No.2N component was quantitatively determined to be 9.5% by weight, using reverse phase liquid-liquid chromatography. The method for Epoxide No.2N required the use of a Waters Associates instrument modified to accommodate a Schoeffel variable wave length UV detector. With this detection system, measurements could be made at a major Epoxide No.2N absorbance band near 280nm. The standard detection system for the Waters instrument measures the UV absorbance at 254nm.

The concentration of Epoxide No.1N obtained by difference is 67.5% by weight. A search failed to reveal an interference-free absorbance band suitable for the direct and independent determination of Epoxide No.1N by infrared techniques.

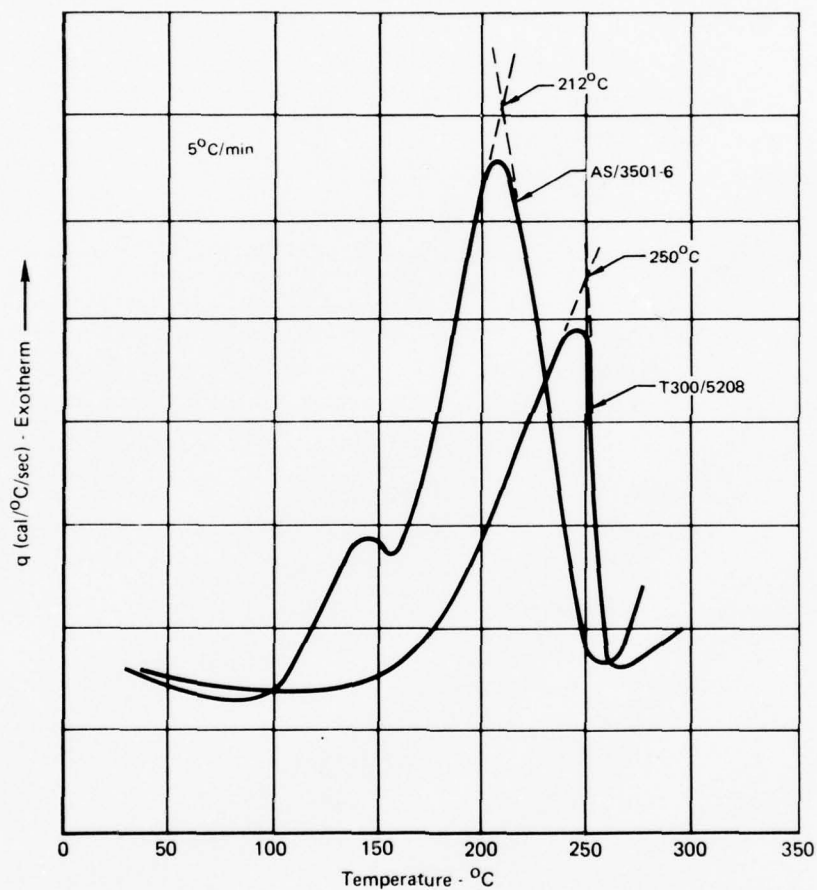
An infrared method was developed for determining the epoxide equivalent/100 grams resin using the absorbance band at 910 cm^{-1} . This method has value for control purposes but cannot be used to determine the weight percent Epoxide No.1N because any prereaction used to advance the resin system to the proper B-stage condition lowers the epoxide concentration. In addition, the extinction coefficient for epoxide concentration varies for different epoxy resins, and where two epoxies are used in a formulation, a proper working curve requires corrections based on a knowledge of the concentration of one of the starting epoxies.

Investigations are continuing toward development of a specific quantitative analytical method for Epoxide No.1N.

4.3 Thermal Analysis and Characterization of 5208

Differential Scanning Calorimetry (DSC) was used for the thermal analysis of the 5208 resin system. The DuPont 990 thermal analyzer was used. In the DSC mode, the instrument records the rate of energy released or absorbed as a function of temperature at a selected linear heating rate.

Figure 7 shows the DSC thermograms for typical batches of T300/5208 and AS/3501-6 graphite/epoxy prepreg at a heating rate of $5^{\circ}\text{C}/\text{min}$. The "thermal signature" obtained for these thermosetting resins is a valuable control tool. Differences in chemical formulation can be detected between different resin systems as well as changes between batches of the same resin. For example, the 3501-6 has a boron trifluoride catalyst and the general exothermal cure



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FIGURE 7
DSC THERMOGRAMS FOR AS/3501-6 AND
T300/5208 GRAPHITE/EPOXY PREPREG

reaction is shown to reach maximum rate (exotherm peak) ahead of the uncatalyzed 5208. The small preliminary exotherm (shown at about 135°C) is characteristic of the 3501-6 and is not noted for thermograms of 5208 or the 3501-5 resin. The effects noted for variations in the chemical composition on batches of the same resin is shown in the subsequent section on the testing of special batches.

It is also possible to detect changes in the stoichiometry of starting materials.

The exotherm peak temperature for a given heating rate, shown as 250°C for 5208 in Figure 7, is a convenient measurement to use for purposes of quality control. The exotherm peak temperatures for a series of DSC runs at different heating rates are related by the following Arrhenius relationship:

$$\log \emptyset = A/T + B$$

Where:

\emptyset = Heating rate (°C/Min)

T = Temperature (°K)

A = Constant, related to activation energy

B = Constant, related to the Arrhenius frequency factor

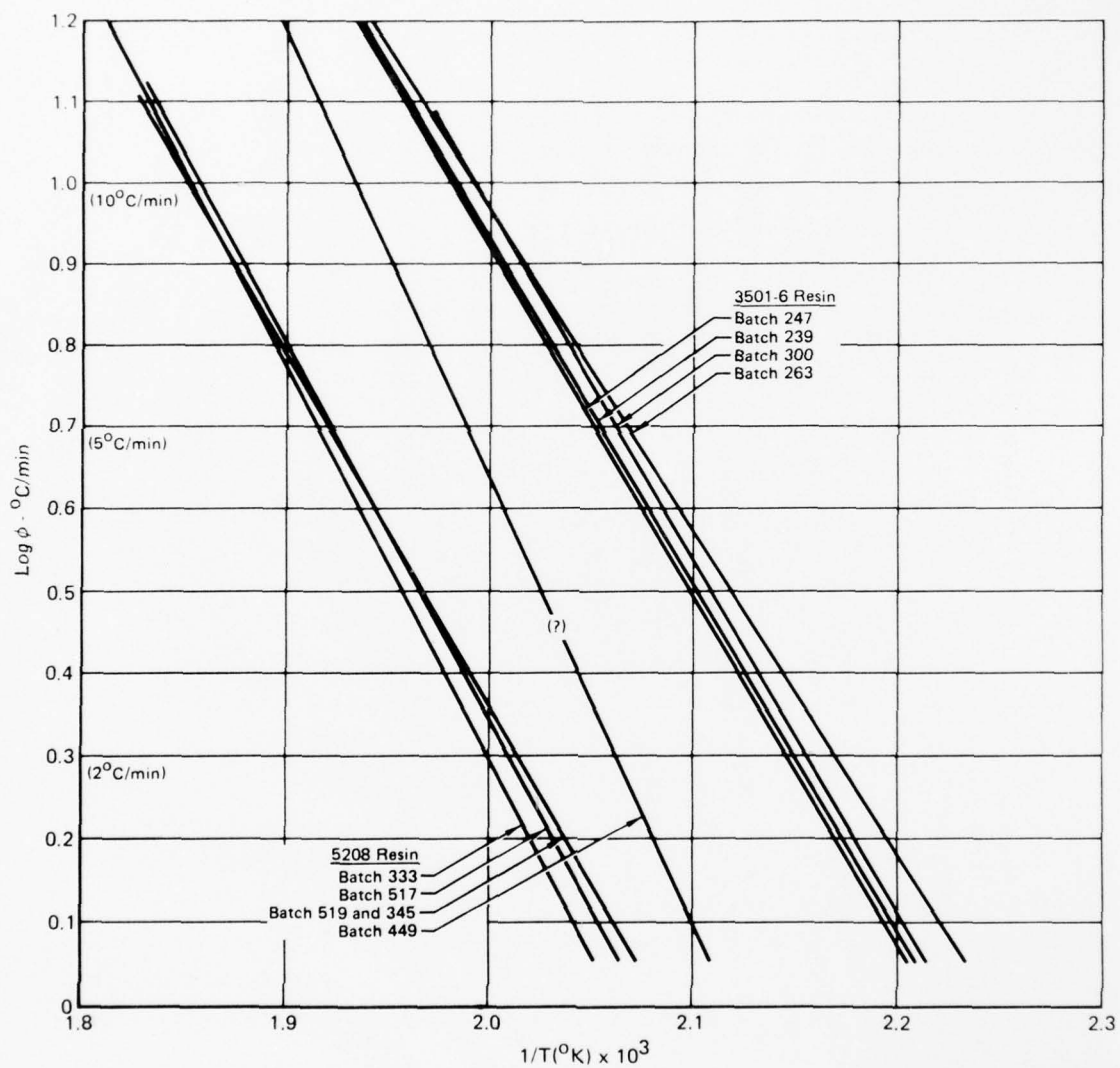
Figure 8 shows the data plots for 5 batches of T300/5208 prepreg and four batches of AS/3501-6. Batch 449 for 5208 does not fall within the family of curves shown for the other batches. It was determined that this batch had a longer or higher temperature B-stage treatment than the other production batches of 5208. The degree of resin advancement can have a definite effect on the tack, handling and processability of the prepreg batch.

4.4 Testing of Production Batches of 5208

Five batches of production T300/5208 were supplied by the vendor for use in the program.

4.4.1 Curing Agent - The five batches of T300/5208 prepreg were analyzed in duplicate for the sulfone curing agent by the quantitative IR method given in the Appendix. The percent curing agent, reported on a resin-matrix basis, is given in Table 2.

4.4.2 Epoxide Concentration - The epoxide concentration was determined in duplicate for four batches of T300/5208 prepreg by the infrared method described in the Appendix with the working curve calculations corrected for Epoxide No. 2N. The epoxide concentration for the resin system was also determined by reacting the epoxide with hydrochloric acid (HCl) and back titrating the unreacted HCl with standardized base solution, Reference (3). The results



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FIGURE 8
DSC DATA PLOTS; AS/3501-6 AND T300/5208 GRAPHITE/EPOXY PREPREG
Heat Up Rate vs Exotherm Peak Temperature

expressed as equivalents/100 grams resin and as weight per epoxide (WPE) are given in Table 3.

TABLE 2
PERCENT CURING AGENT IN T300/5208 PREPREG RESIN

<u>Batch No.</u>	<u>Percent Curing Agent (DDS)</u>
B-333	22.5 (22.9, 22.1)
B-345	22.5 (22.9, 22.1)
B-449	22.6 (22.9, 22.2)
B-517	23.2 (22.8, 23.7)
B-519	23.6 (23.2, 23.9)
Average	22.9
Standard Deviation	± 0.6

The IR and HCl titration methods for WPE give an average value of 184 for the 5208 resin formulation. Calculations, based on typical values of Epoxide No. 1N and Epoxide No. 2N, gives a WPE of 171 for an unreacted mixture of the two epoxies and curing agent. The higher WPE of 184 for 5208 is a measure of the degree of resin advancement during the formulation of the prepreg.

4.4.3 Minor Epoxy Component - The concentration of the minor epoxy, Epoxide No. 2N, was determined for production batches of 5208 by reverse phase liquid-liquid chromatography. The results are given in Table 4.

TABLE 4
EPOXIDE NO. 2N CONCENTRATION FOR T300/5208 PREPREG RESIN

<u>Batch No.</u>	<u>Percent Epoxide No. 2N (Wt.)</u>
B-333	10.9
B-345	9.0
B-449	10.3
B-517	10.8
B-519	<u>9.9</u>
Average	10.2
Standard Deviation	± 0.8

For the multiple batch analysis an external standard calculation was used.

TABLE 3
EPOXIDE CONCENTRATION FOR T300/5208 PREPREG RESIN

Batch No.	IR Method		HCl Titration	
	Eq./100 g. Resin	WPE	Eq./100 g. Resin	WPE
333	0.532	188 (187,189)	0.532 (0.510, 0.554)	188 (196,181)
345	-	-	0.543 (0.553, 0.532)	184 (181,188)
449	0.552	181 (185,177)	0.547 (0.548, 0.538)	184 (182,186)
519	0.554	181 (184,176)	-	-
Average	0.546	183	0.541	185
Std. Dev.	+0.013	+4.8	+0.014	+5.1

A Water's 280nm filter system was used for the UV detector.

The analysis value of 9.5% (Wt.) given in Section 4.2 is believed to be more accurate since it represents an average value obtained for the use of both internal and external standard calculations. In addition, the Schoeffer variable wave length UV detector used in the original analytical work gave greater sensitivity than the Water's 280nm filter system.

4.4.4 Thermal Analysis - Five batches of T300/5208 were examined by DSC. The exotherm peak temperatures were recorded for three different heating rates. The data, reduced as described in Section 4.3, is presented in Table 5. The data plots are given in Figure 8.

TABLE 5
DSC EXOTHERM PEAK TEMPERATURES FOR T300/5208 PREPREG RESIN

Batch No.	Temperature (°C)		
	$\phi = 2^{\circ}\text{C/Min}$	$\phi = 5^{\circ}\text{C/Min}$	$\phi = 10^{\circ}\text{C/Min}$
B-333	227	250	266
B-345	223	250	265
B-449	212	229	244
B-517	225	249	265
B-519	223	249	266
Average (W/O B-449)	224.5	249.5	265.5
Standard Deviation (W/O B-449)	1.9	0.6	0.6
Equation	225.0	247.9	266.7

Equation (Linear regression of $\log \phi$ vs. $1/T$):
(Omitting B-449)

$$\log \phi = - \frac{4502.3}{T} + 9.342218$$

$$r^2 = 0.9912 \text{ (statistical curve fit)}$$

The low exotherm peak temperatures shown for Batch 449 are discussed in the next section.

4.5 Testing of Special Batches of 5208

Special batches of 5208, having intentional variations in chemical composition, were supplied by Narmco. The special batches and vendor-quoted variation from their standard production formulation are given in Table 6.

TABLE 6
SPECIAL BATCHES OF 5208 RESIN

<u>Batch No.</u>	<u>Variation from Standard Production</u>
X91-104A	10% increase in curing agent
X91-104B	10% decrease in curing agent
X91-104C	100% increase in minor epoxy component
B-726	Additional B-Staging

4.5.1 Curing Agent - The percent curing agent (DDS) for special batches were determined by the infrared method and by DSC. The DSC method is discussed in Section 4.5.3. The results are tabulated in Table 7.

TABLE 7
PERCENT CURING AGENT IN 5208 SPECIAL BATCHES

<u>Batch No.</u>	<u>Weight Percent Curing Agent (DDS)</u>	
	<u>IR Method</u>	<u>DSC Method</u>
X91-104A	24.1 (24.2, 24.0)	25.0 (24.9, 25.1, 25.0)
X91-104B	20.5 (20.4, 20.5)	21.1 (20.3, 21.0, 22.0)
X91-104C	-	21.1 (20.0, 21.1, 22.7)

If, as assumed, the vendor increased the parts per hundred resin by the percentages given in Table 6, the intended values for curing agent would be 24.7, 21.2, and 21.0 percent by weight for special batches X91-104A, B, and C, respectively. The results indicate satisfactory accuracy and sensitivity by both the IR and DSC methods. The IR method is preferred for general quality control, however, since a batch which has been highly B-staged would give a high result for curing agent by the DSC method.

4.5.2 Epoxide No.2N - The analysis of batch X91-104C by reverse phase liquid-liquid chromatography gave 17.8% by weight. This compared well with 17.3% by weight obtained by calculation, assuming the parts per hundred Epoxide No.2N were increased 100%, from 14 to 28 phr.

4.5.3 Thermal Analysis - To aid in interpreting DSC data and in evaluating the special batches of "off-specification" resins, synthetic mixtures of Epoxide No.1N and CIBA Eporal (DDS) curing agent were prepared for characterization. These components are the major constituents of a number of other popular graphite prepreg resins, and characterization of the synthetic mixtures affords interpretative data of general applicability.

The plot of thermal data obtained from DSC thermograms of the synthetic mixtures are given in Figure 9. As discussed in Section 4.3, the data can be displayed using a plot of the logarithm of the linear heating rate vs. the reciprocal of the absolute temperature. The family of seven (7) curves obtained for mixtures ranging from 0 to 26 percent curing agent are well defined straight lines ($r^2 = 0.99$ statistical fit).

It was found that the DSC data for any given heating rate could be reduced by logarithm regression to allow determination of the percent curing agent. Figure 10 shows the straight-line plot obtained for the regression analysis of data obtained at a heating rate of 5°C/minute. It is noted that the percent curing agent determined by DSC for the 5208 resin is 23 percent, in excellent agreement with the 22.9% obtained using the infrared method. The percent curing agent for a special batch of 3501-6 prepared without the boron fluoride catalyst is shown to be 24% by the DSC method. The infrared determination was 24.1%. The determination of percent curing agent for formulations of Epoxide No.1N and Eporal containing a catalyst, such as boron trifluoride, would give a high result by the DSC method. Boron trifluoride, a Lewis acid, interacts with the epoxide functional group to change the kinetics of the reaction. The shape of the thermogram is changed and the exotherm peak occurs at temperatures lower than equivalent mixtures without the catalyst. Also, the percent curing agent obtained for 5208 by this DSC calculation is affected by the degree of advancement and "overstaged" material gives a high result.

Figure 11(a) shows the DSC data plots for the 5208 special batches X91-104A and X91-104B which were intentionally varied in amounts of curing agent by the vendor and shown by IR analysis to contain 24.1 and 20.5% DDS, respectively.

Figure 11(b) shows the DSC data plots for standard 5208 formulation compared with Batch 726 which was given an extended B-stage cooking step to advance the resin and give lower tack. The DSC data for batch X91-104C, containing double the standard amount of Epoxide No.2N, is compared with the standard batch.

The data plots for Batch X91-104C (double Epoxide No.2N) in Figure 11(b) is practically the same as that shown in Figure 11(a) for Batch X91-104B (-10% curing agent). This is explained by the fact that both formulas contain approximately 21% curing agent. The DSC data for Batch 726 which was given an

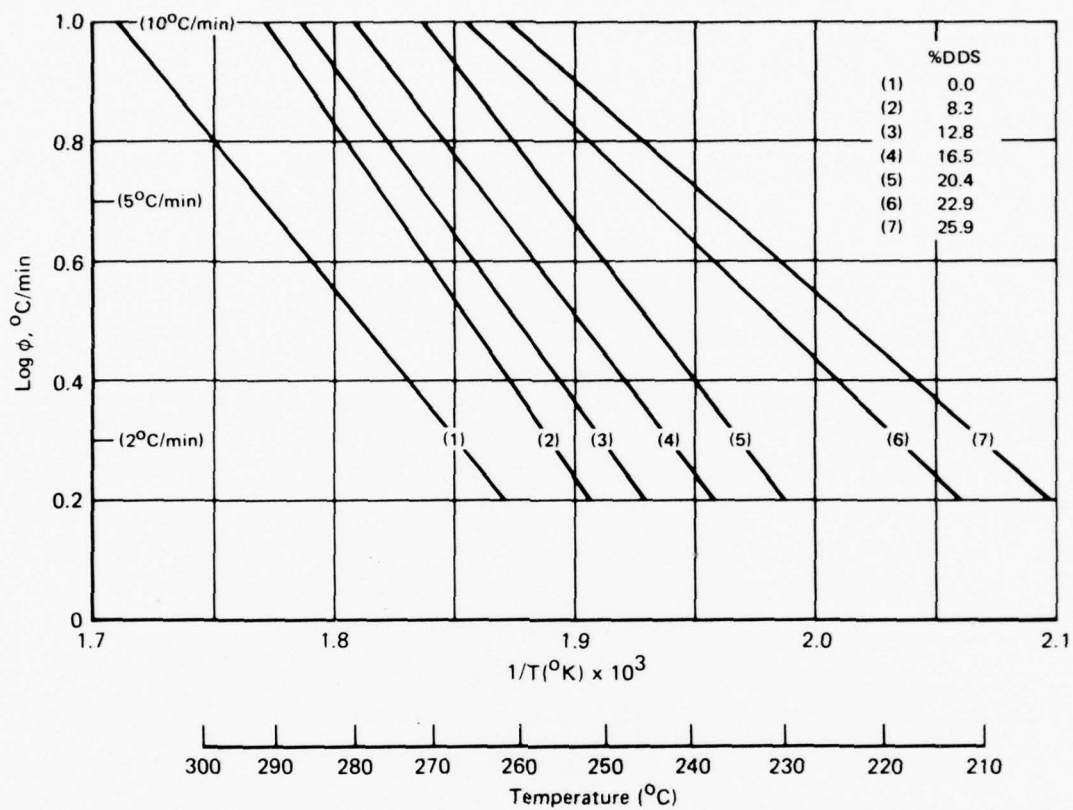
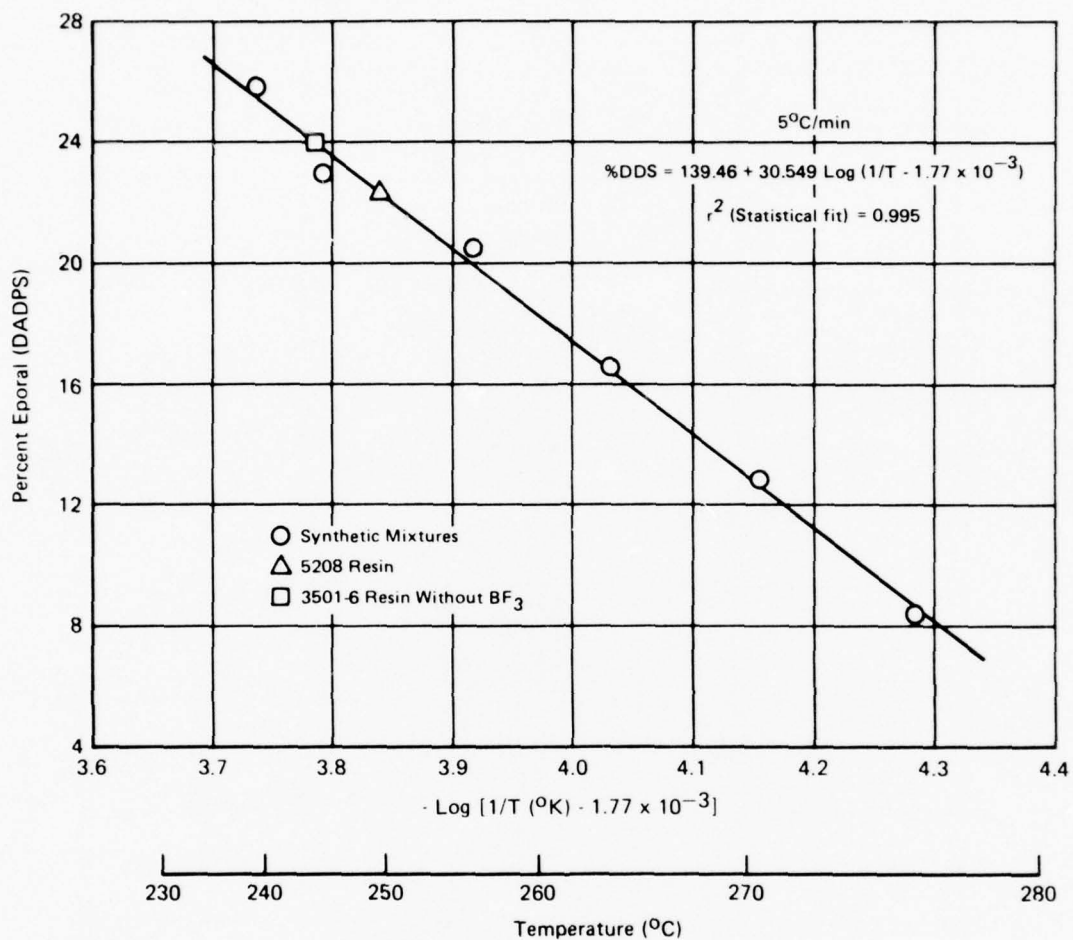


FIGURE 9
DSC DATA PLOTS; SYNTHETIC MIXTURES OF EPOXIDE NO. 1(N) AND DDS
HEAT UP RATE (ϕ) vs EXOTHERM PEAK TEMPERATURE



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FIGURE 10
PERCENT CURING AGENT FROM DSC EXOTHERM PEAK TEMPERATURE :
(EPOXIDE NO. 1(N) + DDS MIXTURES)

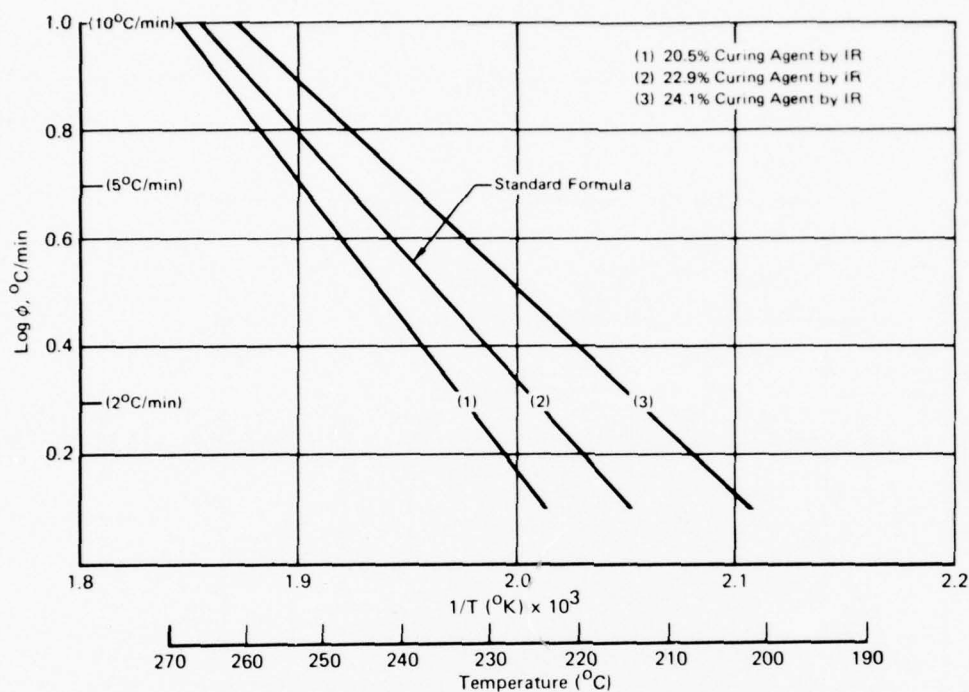


FIGURE 11 (a)

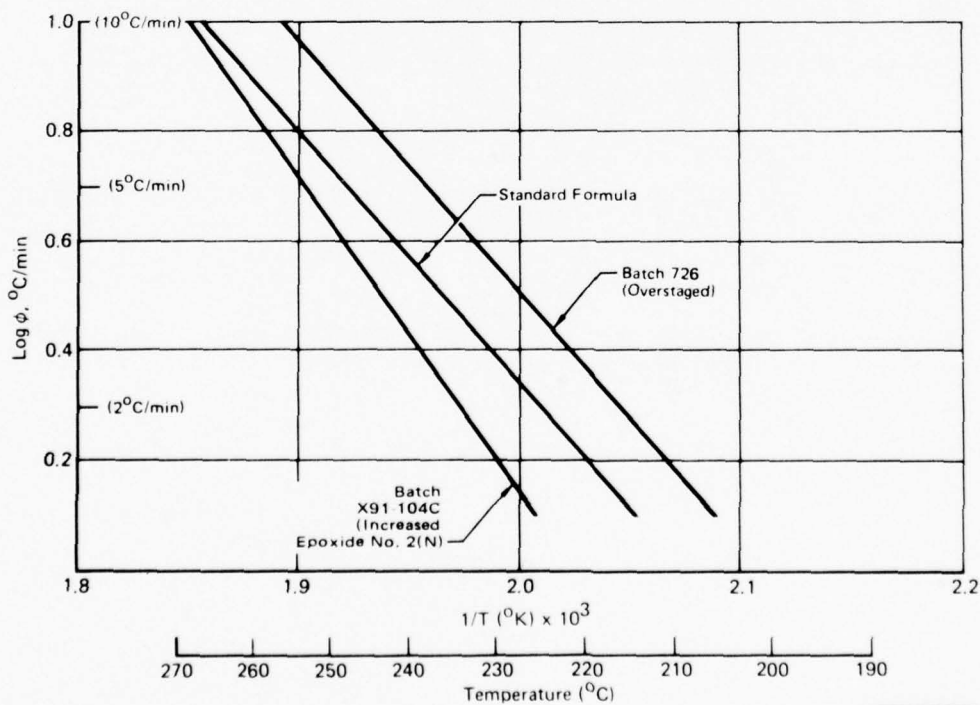


FIGURE 11(b)

DSC DATA PLOTS; 5208 SPECIAL RESIN BATCHES
HEAT UP RATE vs EXOTHERM PEAK TEMPERATURE

extra long B-stage cook time, indicates that Batch 449 (DSC data shown in Section 4.3, Figure 8) was probably an overstaged production batch.

4.6 Recommended Acceptance Criteria for T300/5208 Prepreg

Table 8 lists the physiochemical tests and limits recommended for receiving quality control for T300/5208 prepreg.

TABLE 8
PHYSIOCHEMICAL QUALITY CONTROL OF T300/5208 PREPREG

<u>Properties of Uncured Prepreg (Resin Basis)</u>	<u>Requirements (Per Methods in Appendix)</u>
Curing Agent (Wt.%)	21 - 25
Minor Epoxy (Wt.%)	7 - 13
Weight per Epoxide (WPE)	170 - 200
DSC (Exotherm peak temperature, °C at 5°C/Min.)	245 - 255

The rather broad spread in the acceptance limits reflects statistical treatment of the data to encompass 99% of the expected variation at 95% confidence. Provision has been made to routinely store quality control data in a CDC/System 73. The data will be periodically reviewed and limits adjusted to reflect the increased data base.

5. HERCULES AS/3501-6 GRAPHITE/EPOXY PREPREG

5.1 Resin Analysis for 3501-6

The quantitative analysis of 3501-6 resin is given in Table 9.

TABLE 9
ANALYSIS OF 3501-6 RESIN

<u>Component</u>	<u>Analysis</u>	
	<u>Parts/100 resin</u> <u>(phr)</u>	<u>Percent</u> <u>(Wt.)</u>
Epoxide No.1H	100	56.5
CIBA Eporal (Curing Agent)	44	24.9
Epoxide No.2H	16	9.0
Epoxide No.3H	15	8.5
Boron Trifluoride Complex (Catalyst)	2	1.1

The formulation given in Table 9 was supplied by Hercules and greatly reduced the amount of analytical testing time required.

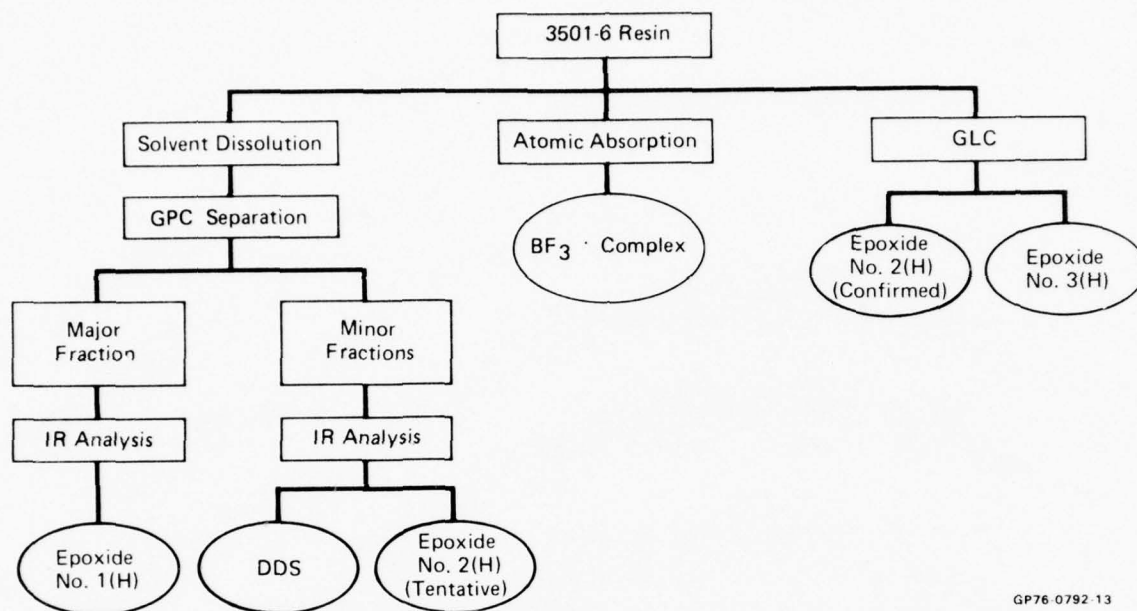
5.2 Identification and Quantitative Determination of 3501-6 Components

The schematic for 3501-6 resin separation and component identification is given in Figure 12.

The two major components, Epoxide No.1H and CIBA Eporal (DDS), were identified by infrared analysis of the fractions obtained using gel permeation chromatography (GPC). The concentration of curing agent was determined as 24% by weight using the infrared technique. A split of the major Epoxide No.1H fraction showed IR absorbance bands indicating the possible presence of Epoxide No.2H, particularly the carbonyl band at 5.8 micrometers. The presence of the Epoxide No.2H component was verified by using gas-liquid chromatography (GLC).

For the GLC identification, acetone solutions of the resin samples were analyzed on special columns packed with Dextsil 300, a stationary phase that does not lose its efficiency when operated at sustained high temperatures. The GLC conditions used for the analysis are as follows:

Vaporizer Temperature	= 280°C
Initial Column Temperature	= 175°C (Hold for 1 minute)
Final Column Temperature	= 250°C (Hold until analysis complete)
Column Temperature Rise-Rate	= 15°C/Minute
Flame Ionization Detector Temperature	= 250°C
Sample Size	= 5.0 ul of acetone solution containing 40 ug of polymer/ul.



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FIGURE 12
SEPARATION AND IDENTIFICATION OF 3501-6 RESIN COMPONENTS

The chromatogram obtained for the Epoxide No. 2H, under the GLC conditions listed above, consisted of a series of three doublets eluting at four minutes, six minutes (the major doublet) and eight minutes. Thus, six peaks instead of one are used to characterize the Epoxide No. 2H. The Epoxide No. 1H used in the 3501-6 resin was analyzed by GLC under the same conditions and no peaks of any kind were observed for the first 16-minutes of the analysis. Further, any free curing agent present in the 3501-6 resin would not yield interfering peaks, as polyfunctional amines such as DDS will generally decompose when being passed through a stainless steel GLC column at temperatures about 200°C.

Gas-liquid chromatograms that establish presence of Epoxide No. 2H in the 3501-6 are shown in Figure 13. The concentration of Epoxide No. 2H was determined by infrared, using the carbonyl band, to be 9.2% by weight. The actual percent Epoxide No. 2H in the Hercules formulation is 9.0%.

Epoxide No. 3H was identified as a component in 3501-6 by noting two prominent peaks in the GLC analysis of the resin with elution times at 10.6 and 12.6 minutes. An acetone solution of Epoxide No. 3H was analyzed by GLC and the location of two of the major peaks established the identity of the second minor epoxy, as shown in Figure 14. A quantitative GLC method was developed for Epoxide No. 3H. The detailed method is given in the Appendix. This method gives a concentration of 6% by weight. It was determined that 6% was actually the "free" Epoxide No. 3H, leaving 2.5% by weight of the Epoxide No. 3H present in a combined form with the curing agent. A boron trifluoride catalyst was identified using atomic absorption. Quantitative determination of boron by atomic absorption shows a concentration of 0.8-1.2% as an organic complex of BF_3 .

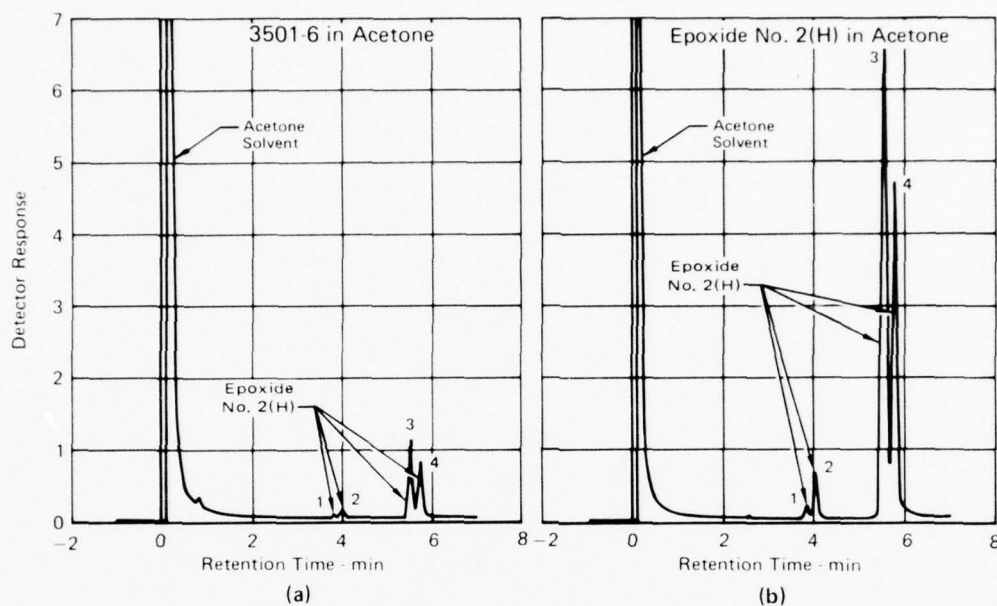
Epoxide No. 1H by difference, using a "free" Epoxide No. 3H value of 6% gives 59% by weight. The need to complete the development of a direct method for quantitative analysis of Epoxide No. 1H was noted in Section 4.

5.3 Thermal Analysis and Characterization of 3501-6 Resin

The DSC thermogram for 3501-6 at a heating rate of 5°C/min is shown in Figure 15. The preliminary exotherm at 135°C followed by the major exotherm peak at 212°C identified the material as 3501-6.

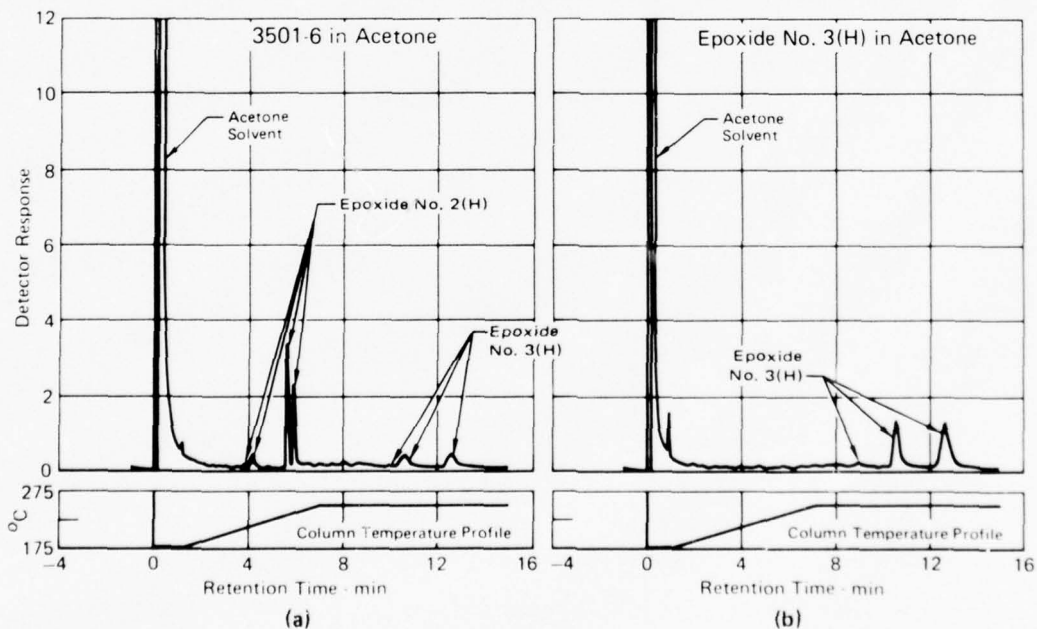
The small preliminary exotherm is associated with the boron trifluoride organocomplex used as a catalyst. The heating rate (\emptyset), °C/min., is related to the absolute temperature (T), °K, by the following Arrhenius expression:

$$\log \emptyset = - \frac{3635.0}{T} + 9.57780$$



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FIGURE 13
IDENTIFICATION OF MINOR EPOXY COMPONENT IN 3501-6 RESIN
BY GAS PHASE CHROMATOGRAPHY



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FIGURE 14
IDENTIFICATION OF SECOND MINOR EPOXY COMPONENT IN 3501-6 RESIN
BY GAS PHASE CHROMATOGRAPHY

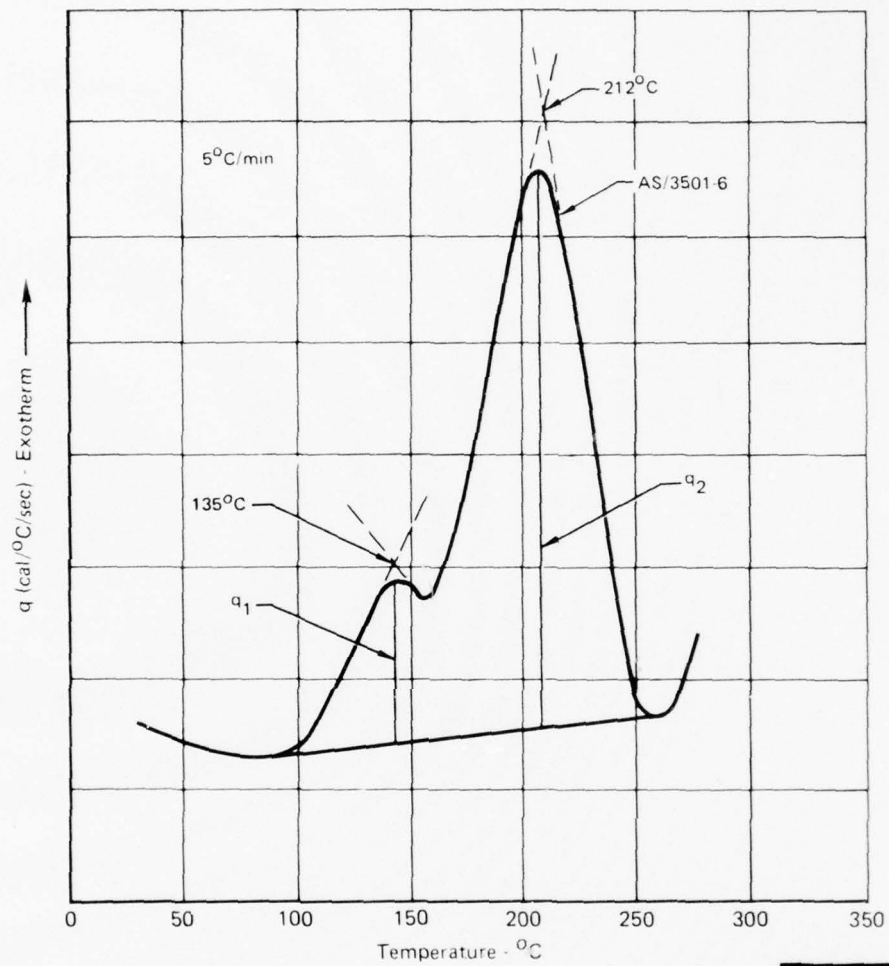


FIGURE 15
DSC THERMOGRAMS FOR AS/3501-6

The expression for the major exotherm peak data is given by:

$$\log \emptyset = - \frac{4053.2}{T} + 9.042454$$

The data for three heating rates are given in Table 10.

TABLE 10
DSC MAJOR AND MINOR PEAK TEMPERATURES FOR 3501-6 RESIN

	Temperature (°C)		
	$\emptyset = 2^{\circ}\text{C/Min}$	$\emptyset = 5^{\circ}\text{C/Min}$	$\emptyset = 10^{\circ}\text{C/Min}$
Major Peak	191	212	231
Minor Peak	119	135	151

Preliminary tests with synthetic mixtures indicate that a concentration level for the catalyst, suitable for quality control, can be obtained by ratioing the peak heights (q_1/q_2 , Figure 15). This would obviate the need for a separate control test to determine boron by atomic absorption.

Narmco 5208 does not contain a boron trifluoride accelerator and does not show the preliminary minor exotherm. Hercules 3501-5, which does contain a boron trifluoride catalyst, shows a preliminary peak at lower heating rates. For higher heating rates the preliminary exotherm for 3501-5 is obscured by the overall reaction exotherm.

5.4 Testing of Production Batches of 3501-6

Four production batches of AS/3501-6 prepreg were supplied by the vendor for use in the program. The neat (bulk) resin for three of these batches were also available for test.

5.4.1 Curing Agent - The prepreg and neat resin batches were analyzed in duplicate for the sulfone curing agent by the infrared method given in the Appendix. The data for weight percent curing agent is given in Table 11.

TABLE 11
PERCENT CURING AGENT IN 3501-6
NEAT RESIN AND AS/3501-6 PREPREG RESIN

<u>Batch No.</u>	<u>Percent Curing Agent (DDS)</u>
B-239 (prepreg)	23.3 (23.5, 23.1)
(neat resin)	23.3 (23.7, 22.9)
B-247 (prepreg)	24.3 (24.4, 24.2)
(neat resin)	24.2 (24.1, 24.3)
B-263 (prepreg)	23.8 (23.0, 24.6)
(neat resin)	23.2 (23.4, 23.0)
B-300 (prepreg)	23.2 (23.3, 23.0)
Average	23.6
Standard Deviation	± 0.6

It is noted that the percent DDS obtained by infrared gives an average value of 23.6% compared to the Hercules formulation value of 24.9%.

5.4.2 Epoxide Concentration - The epoxide concentration was determined in duplicate for four batches of AS/3501-6 prepreg and three batches of neat resin. The infrared method was used, with the equivalents per 100 grams resin taken directly from a working curve based on standard solutions prepared from Epoxide No. 1H. The results are given in Table 12.

TABLE 12
EPOXIDE CONCENTRATION FOR 3501-6 RESIN⁽¹⁾

<u>Batch No.</u>	<u>Eq/100g Resin</u>	<u>WPE</u>
B-239 (prepreg)	0.422 (0.422, 0.421)	237 (237, 237)
(neat resin)	0.475 (0.486, 0.464)	212 (208, 216)
B-249 (prepreg)	-	-
(neat resin)	0.492 (0.491, 0.494)	203 (204, 202)
B-263 (prepreg)	0.459 (0.442, 0.477)	218 (226, 210)
(neat resin)	0.475 (0.474, 0.477)	210 (211, 209)
B-300 (prepreg)	0.481 (0.485, 0.477)	209 (208, 210)
(neat resin)	-	-
Average	0.467	215
Standard Deviation	± 0.025	± 12

(1) IR Method using Epoxide No. 1H standard solutions

By taking the data directly from a working curve prepared from Epoxide No. 1H, the equivalents/100 grams resin reported are higher than the true value (WPE lower than the true value).

The fact that the IR extinction coefficients differ for all three epoxies present, considerably reduces the value of the IR method for a quality control method for epoxide concentration of 3501-6. The possibility exists that a given batch could have compensating errors in formulation that would give an acceptable WPE for a rejectable batch.

5.4.3 Epoxide No. 2H - The concentration of the minor epoxy additive, Epoxide No. 2H, was determined for production batches of 3501-6 prepreg resin and neat resins by infrared using the carbonyl absorbance band. The data is given in Table 13.

TABLE 13
EPOXIDE NO. 2H CONCENTRATION FOR 3501-6 RESIN

<u>Batch No.</u>	<u>Percent (Wt.) CY179</u>
B-239 (neat resin)	9.72 (9.79, 9.66)
B-247 (neat resin)	9.72 (9.81, 9.64)
B-263 (prepreg)	8.56 (8.24, 8.89)
(neat resin)	9.71 (9.76, 9.66)
B-300 (prepreg)	9.13 (9.09, 9.17)
B-421 (prepreg)	<u>8.61</u> (8.42, 8.80)
Average	9.24
Standard Deviation	± 0.56

Hercules used the same method to determine Epoxide No. 2H for 15 resin samples representing three different resin batches. Hercules test results ranged from 8.8 to 9.0 weight percent Epoxide No. 2H.

5.4.4 Epoxide No. 3H - A method for determining the total amount of Epoxide No. 3H used in formulating the resin was not found. The GLC method for Epoxide No. 3H determines the "free" Epoxide No. 3H. Values obtained for uncombined Epoxide No. 3H are given in Section 5.5.

5.4.5 Thermal Analysis - Four batches of production prepreg and three of the neat resin were examined by DSC. The data is given in Table 14. The data plots are shown in Figure 8.

TABLE 14
DSC EXOTHERM PEAK TEMPERATURES FOR AS/3501-6 RESIN

Batch No.	Temperature (°C)		
	$\emptyset = 2^{\circ}\text{C/Min}$	$\emptyset = 5^{\circ}\text{C/Min}$	$\emptyset = 10^{\circ}\text{C/Min}$
B-239 (prepreg)	193	213	232
(neat resin)	190	210	230
B-247 (prepreg)	193	215	232
(neat resin)	193	213	232
B-263 (prepreg)	188	210	230
(neat resin)	194	214	232
B-300 (prepreg)	187	212	228
Average	191	212	231
Standard Deviation	± 2.8	± 1.9	± 1.6
Equation	191	213	231

Equation (Linear Regression of $\log \emptyset$ vs $1/T$)

$$\log \emptyset = - \frac{4053.2}{T} + 9.042454$$

$$r^2 = 0.984 \text{ (statistical curve fit)}$$

5.5 Testing of Special Batches of 3501-6

Special batches of 3501-6 resin having intentional variations in chemical composition were supplied by Hercules. The special batches and vendor-quoted variation from their standard production formulation are given in Table 15.

TABLE 15
COMPOSITION OF SPECIAL BATCHES OF 3501-6 RESIN

<u>Group No.</u>	<u>Batch Nos.</u>	<u>Variation from Standard Production</u>
(1)	B-1,6,8,9,10	Standard Formula
(2)	B-2,4,5,7,11	Without BF_3 Complex
(3)	B-3	Without BF_3 Complex and Epoxide No.3H

5.5.1 Chemical Testing - The special batches of 3501-6 were tested for percent curing agent (DDG), catalyst (BF_3 Complex) and epoxide concentration (WPE). The results together with amount added, as reported by the vendor, are given in Table 16. Determinations were also made for the minor epoxy components

Epoxide No.2H and Epoxide No.3H, using GLC. The results are given in Table 17. The GLC detects only the "free" or unreacted amounts of these components. It appears that more Epoxide No.3H has reacted during the formulation of the standard material than for the formulation of batches without catalyst addition.

5.5.2 Thermal Analysis - DSC thermograms were run at three heating rates for the special batches of 3501-6. Data plots are shown in Figure 16.

TABLE 16

CHEMICAL TEST RESULTS FOR SPECIAL BATCHES OF 3501-6

Batch Description	Catalyst (Wt.%)		Curing Agent (Wt.%)		Epoxide (WPE)	
	Added	Found	Added	Found	Added (1)	Found (2)
Group (1) - Standard (Avg. of 10 Determinations)	1.1	1.2	24.9	24.2	178	203
Group (2) - W/O BF ₃ (Avg. of 10 Determinations)	0.0	0.2	25.2	24.4	177	185
Group (3) - W/O BF ₃ and Epoxide No. 3H (Avg. of 2 Determinations)	0.0	0.2	27.6	27.6	175	173
(1) Calculated from Starting Materials (No advancement)						
(2) Epoxide No. 1 Basis						

TABLE 17

DETERMINATION OF MINOR EPOXIES IN SPECIAL BATCHES OF 3501-6

Batch Description	Wt. % Free		Wt. % Combined		Wt. % Free		Wt. % Combined	
	Epoxide No. 2H (GLC)	Epoxide No. 2H (By Diff.)	Epoxide No. 2H (GLC)	Epoxide No. 2H (By Diff.)	Epoxide No. 3H (GLC)	Epoxide No. 3H (By Diff.)	Epoxide No. 3H (GLC)	Epoxide No. 3H (By Diff.)
Group (1) (Standard Formulation)	3.4	5.6	5.1	3.4				
Group (2) (Formulation W/O BF ₃)	2.8	6.3	6.0	2.6				
Group (3) (W/O BF ₃ and W/O Epoxide No. 3H)	2.9	7.1	0.0	0.0				



5.6 Recommended Acceptance Criteria for 3501-6 Prepreg

Table 18 lists the physiochemical tests and limits recommended for receiving quality control for 3501-6 prepreg.

TABLE 18
PHYSIOCHEMICAL QUALITY CONTROL OF 3501-6 PREPREG

<u>Properties of Uncured Prepreg (Resin Basis)</u>	<u>Requirements (Per Methods in Appendix)</u>
Curing Agent (Wt.%)	23 - 27
Boron Trifluoride Catalyst (Wt.%)	0.8 - 1.6
Weight Per Epoxide (WPE)	160 - 280
Epoxide No. 2H, (Wt.%)	8 - 10
Epoxide No. 3H, (Wt.%)	to be determined
DSC (Exotherm Peak Temperature, °C at 5°C/Min)	202 - 222

6. AMERICAN CYANAMID FM400 ADHESIVE

6.1 Resin System Analysis for FM400

The quantitative analysis of the FM400 resin system is given in Table 19.

TABLE 19
ANALYSIS OF FM400 RESIN SYSTEM

Component	Analysis	
	Parts/100 Resin (phr)	Percent (Wt.)
Epoxide No.1A	100	35.3
Dicyandiamide (DICY)	11	3.9
Metal Powder	160	56.5
Silicate-Type Filler	12	4.2

The FM400 adhesive film, as supplied by the vendor, is supported by a nylon tricot scrim, amounting to approximately 7% by weight.

6.2 Identification and Quantitative Determination of FM400 Components

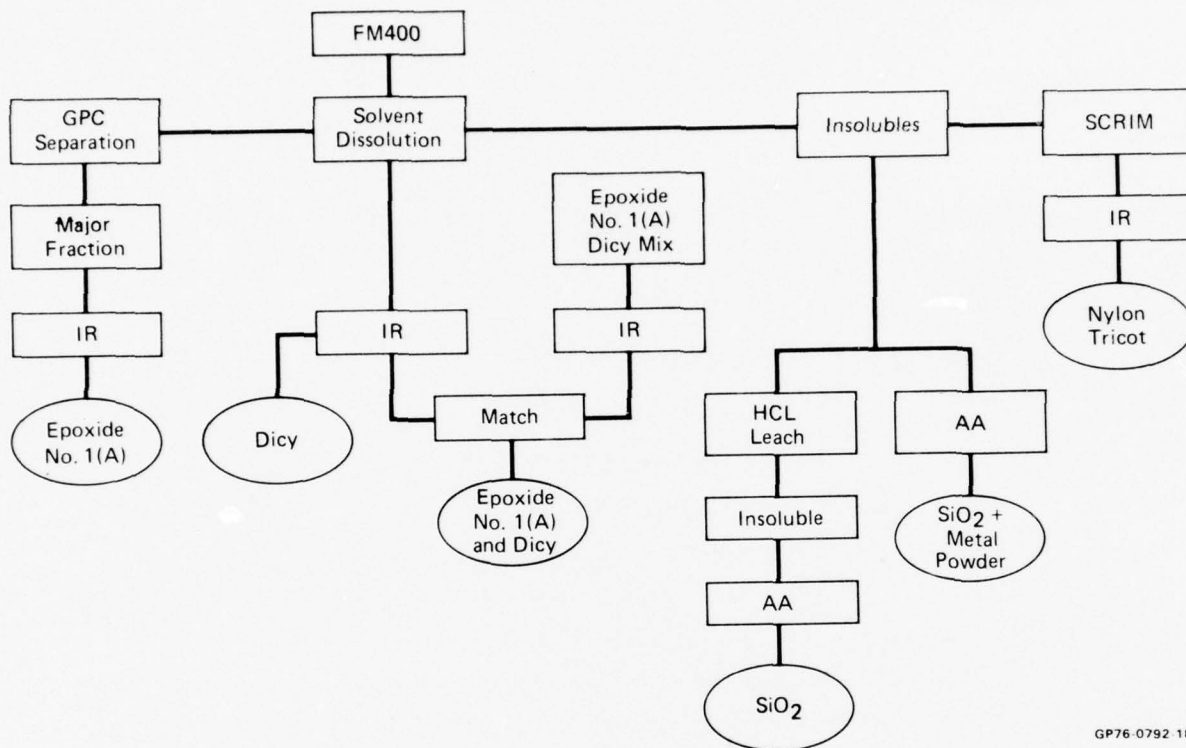
The schematic for FM400 resin system separation and component identification is given in Figure 17.

For the FM400 analysis the solvent soluble portion was separated by gel permeation chromatography on the basis of molecular size and found to contain a single epoxy resin, identified by IR as Epoxide No.1A. The curing agent was identified and quantitatively determined by infrared as dicyandiamide (DICY). The quantitative amount of Epoxide No.1A was then determined by difference and checked by a standard wet method analysis using a hydrogen bromide/acetic acid titration technique. The nylon scrim was physically separated (tweezers) and identified by IR and softening point to be nylon tricot. Atomic absorption (AA) was used to identify the remaining insolubles as metal powder and a silicate-type filler. The metal powder was separated from the filler by an acid leach and quantitatively determined by difference. The remaining silicate-type filler was ignited and weighed and the amount quantitatively established.

A synthetic mixture of Epoxide No.1A and DICY gives an excellent IR match with the FM400 resin system, Figure 18. The investigator should be aware, however, that minor epoxy additives, particularly the EPN and ECN novolacs can be obscured by the absorbance bands from Epoxide No.1A.

6.3 Thermal Analysis and Characterization of FM400

The DSC thermograms for FM400 at heating rates of 2 and 10°C/min is shown in Figure 19. DICY cured systems exotherm more rapidly than the sulfone (DDS) cured systems, once reaction is initiated.



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FIGURE 17
SEPARATION AND IDENTIFICATION OF FM400 COMPONENTS

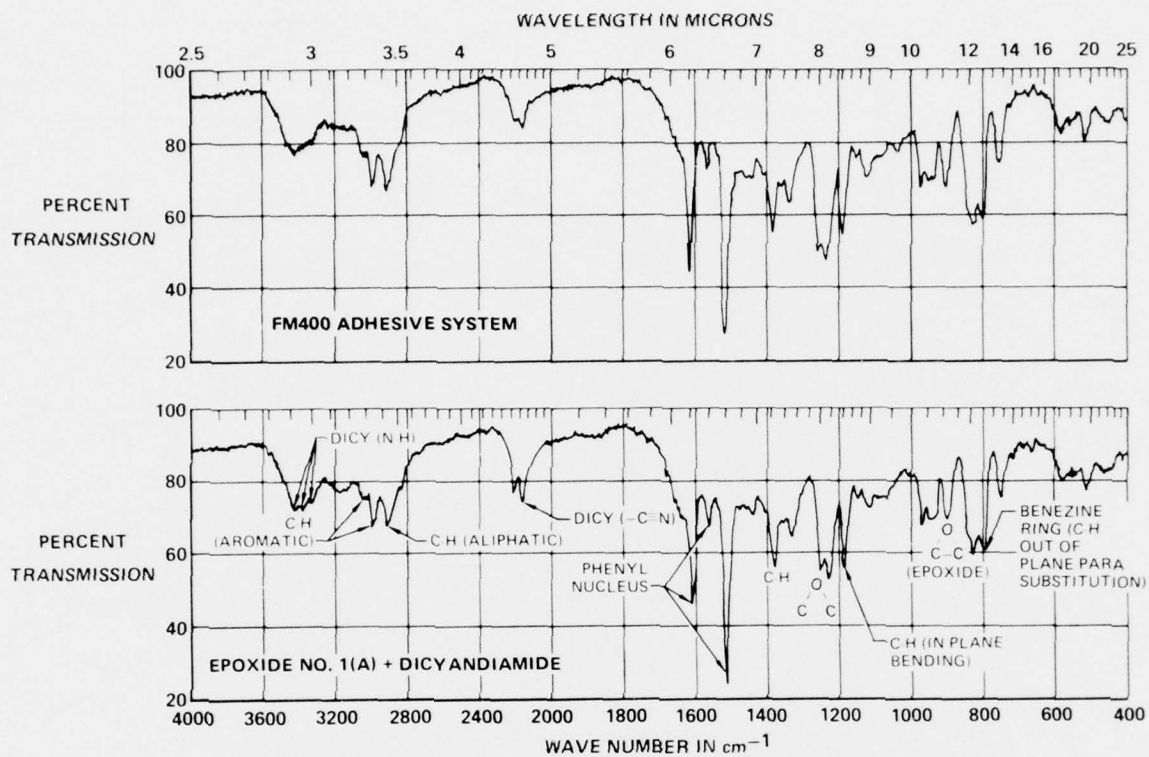


FIGURE 18
INFRARED IDENTIFICATION CHECK OF FM400 RESIN SYSTEM USING
SYNTHETIC MIXTURE

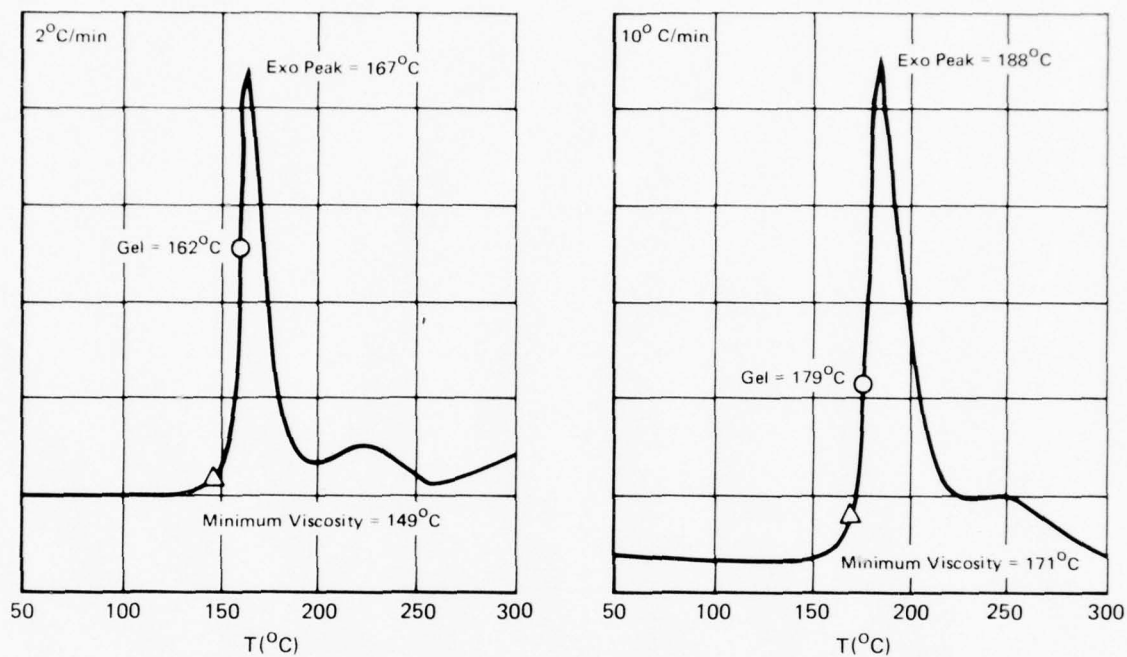


FIGURE 19
DSC THERMOGRAMS FOR FM 400 RESIN:
(INDICATING MINIMUM VISCOSITY AND GEL POINTS)

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Viscosity profiles were determined for bulk FM400 for the same heating rates used for the DSC thermograms. At all heating rates, minimum resin viscosity is obtained just following the start of the reaction exotherm at the "knee" of the curve. At this point, the drop in viscosity due to temperature rise is overridden by an increase in viscosity due to polymerization. The temperature for gel, at all heating rates, occurred at the mid-point between reaction on-set and the exotherm peak temperatures as shown in Figure 19. The relationship between viscosity (flow characteristics) and the DSC-monitored reaction exotherm adds to the importance of obtaining the "thermal signature" as a part of the quality control acceptance testing. Correlation of DSC data with rheological properties of the resin melt is described in detail in Reference (4).

The thermograms shown in Figure 19 were made using the bulk (neat) resin. Similar thermograms for the supported film, show a small endotherm at the melting point of the nylon tricot scrim. The endotherm does not vary with heating rate and constitutes a useful control check for the use of the proper support scrim.

6.4 Testing of Production Batches of FM400

6.4.1 Chemical Control Testing - Previous in-house testing directed toward establishing chemical acceptance criteria for FM400 included percent curing agent (DICY) and epoxide ratio by quantitative infrared methods and percent water by gas phase chromatography. Limits for the acceptance tests were established from the MCAIR data given in Table 20, together with the results obtained by American Cyanamid in a joint test program.

TABLE 20
CHEMICAL CONTROL TESTS FOR FM400 PRODUCTION BATCHES

BATCH NO.	PERCENT DICY (Wt.) (AVG. OF 2)	EPOXIDE RATIO (AVG. OF 8)	PERCENT WATER (Wt.) (AVG. OF 5)
B-93	3.42	0.487	0.182
B-96	3.64	0.502	0.246
B-99	3.36	0.486	0.144
B-100	3.71	0.513	0.087
B-102	3.40	0.518	0.120
B-103	3.51	0.515	0.122
B-105	3.38	0.523	0.083
B-106	3.66	0.517	0.104
BX-3022	3.24	0.507	0.218
BX-3023	<u>3.35</u>	<u>0.508</u>	<u>0.311</u>
AVERAGE	3.47	0.508	0.162
STANDARD DEV.	+0.16	+0.0354	+0.05

The epoxy is controlled by an infrared internal standard technique whereby the epoxide (oxirane) absorbance at 910cm^{-1} is divided by the absorbance of an internal standard at 800cm^{-1} . This gives a practical quantitative control of the epoxide functionally without requiring direct analysis for the percent Epoxide No. 1A. The percent dicyandiamide (DICY) is readily measured by a quantitative IR liquid cell technique using the interference-free absorbance band at 2190cm^{-1} . The percent water is included as part of the chemical control testing, since high moisture content in the adhesive film can cause poor high temperature mechanical properties. The chemical test methods are given in the Appendix.

6.4.2 Thermal Analysis - Five production batches of FM400 adhesive film were compared by differential scanning calorimetry (DSC) using the DuPont 990 thermal analyzer. Data plots were obtained for the rate of energy release vs. temperature for three different linear heating rates. The peak temperatures for the exotherms are shown in Table 21. The sets of exotherm peak temperatures obtained at different heating rates obey an Arrhenius relationship and the equation for FM400 data is shown.

The same five batches were tested in duplicate by American Cyanamid's Stamford Laboratory using a DuPont 900 instrument. The Stamford results are shown in Table 22.

TABLE 21

DSC EXOTHERM PEAK TEMPERATURES FOR FM400 ADHESIVE (PERFORMED AT MCAIR)

Batch Number	Temperature (°C)		
	$\phi = 2^\circ\text{C/min}$	$\phi = 5^\circ\text{C/min}$	$\phi = 10^\circ\text{C/min}$
200	167	180	187
201	166.5	178	187
204	166	177	187
208	167	177	188
210	166	177	187
Average	166.5	177.8	187.2
Equation	166.4	178.0	187.1

Equation (Linear regression of $\log \phi$ vs $1/T$)

$$\log \phi = -\frac{6835.84}{T} + 15.857173$$

$$r^2 = 0.9998 \text{ (statistical fit)}$$

TABLE 22

DSC EXOTHERM PEAK TEMPERATURES FOR FM400 ADHESIVE
(PERFORMED AT AMERICAN CYANAMID)

Batch Number	Temperature (°C)		
	$\phi = 2.5^\circ\text{C/min}$	$\phi = 5^\circ\text{C/min}$	$\phi = 10^\circ\text{C/min}$
200	170	178.5	188.5
201	168	178	189
204	170.5	176.5	188
208	169.5	177	189
210	171.5	179	188.5
Average	169.9	177.8	188.6
Equation	169.4	178.6	188.2

Equation

$$\log \phi = -\frac{6542.52}{T} + 15.185214$$

$$r^2 = 0.9940 \text{ (statistical fit)}$$

6.5 Testing of Special Batches of FM400

Special batches of bulk FM400 adhesive were prepared by American Cyanamid. Formulations were prepared with 2.5%, 3.6%, and 4.5% by weight dicyandiamide curing agent.

The curing agent concentration was determined by the methods given in the Appendix, with the results shown in Table 23.

TABLE 23
TEST RESULTS FOR SPECIAL BATCHES OF FM400

Batch No.	Percent Dicyandiamide (Wt.)	
	Added (Vendor)	Found (IR Method)
51-C	4.5	4.50 (4.52, 4.49)
51-A	3.6	3.60 (3.66, 3.53)
51-B	2.5	2.56 (2.61, 2.52)

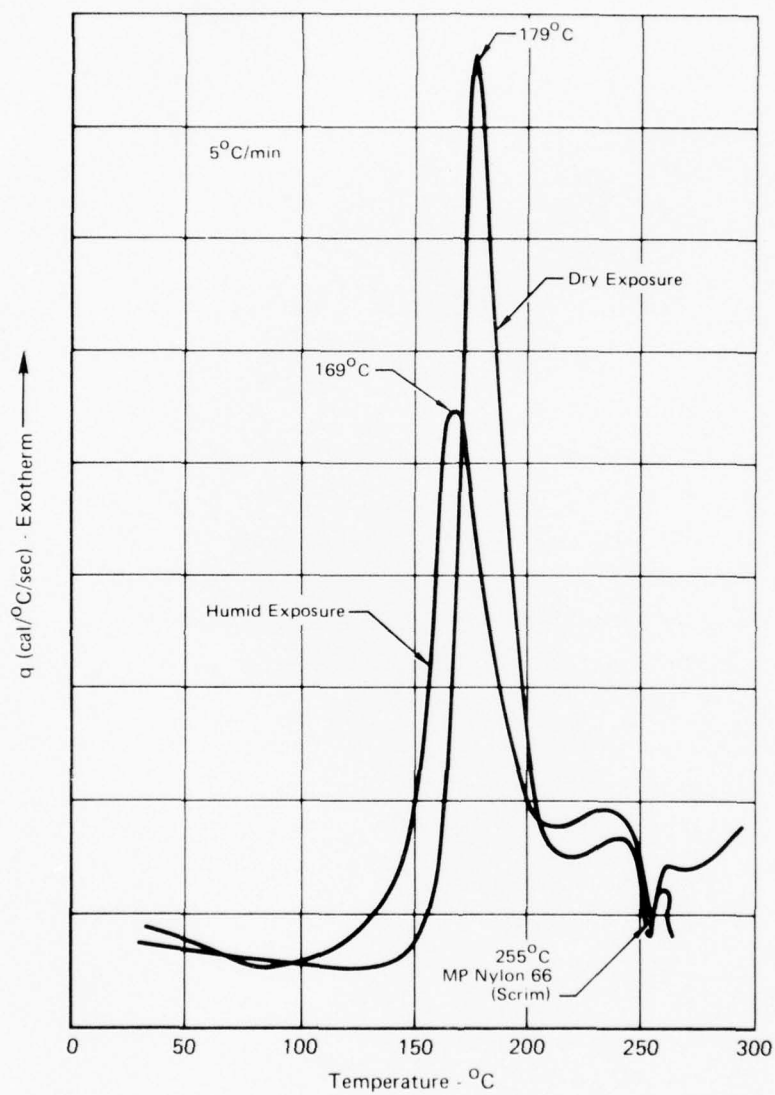
The results of special batch tests for percent curing agent indicate acceptable accuracy and precision for the IR method for dicyandiamide.

6.5.1 Thermal Analysis - Variation in the concentration of the DICY curing agent, at the levels shown in Table 23, caused no significant change in the DSC thermogram. This is in contrast to the sulfone (DDS) cure of the same Epoxide where changes in percent curing agent were readily detected.

To check applicability of DSC techniques for detecting overage material, uncured FM400 adhesive film was exposed to elevated temperatures under both dry (oven) and humid (100%R.H.) conditions. The exposed specimens were tested by DSC. The effect on the DSC thermogram for three days exposure at 140°F under wet and dry conditions is shown in Figure 20. The dry exposure thermogram was not significantly changed from that of the unexposed control. The humid exposure caused a drop in on-set temperature and gave an exotherm peak temperature about 10°C lower than the specimen exposed under dry oven conditions for a heating rate of 5°C/min.

In both thermograms the small endotherm at 255°C is due to the melting of the nylon tricot scrim. The inadvertent use of a low temperature scrim is easily detected.

The DSC data for 3 and 10 day exposures are given in Table 24.



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FIGURE 20
DSC THERMOGRAMS OF FM400
(EXPOSED: 140°F, DRY AND 140°F, 100% RH FOR 3 DAYS)

TABLE 24

DSC DATA FOR FM400 EXPOSED TO ELEVATED TEMPERATURE AT LOW AND HIGH HUMIDITY

Specimen Description	EXOTHERM PEAK TEMPERATURE (°C)		
	$\phi = 2^\circ\text{C/Min.}$	$\phi = 5^\circ\text{C/Min}$	$\phi = 10^\circ\text{C/Min}$
1. Unexposed, Control	166	178	187
2. Exposed, 3 days, 140°F, Dry	167	179	188
3. Exposed, 3 days, 140°F, 100%RH	155	169	180
4. Exposed, 10 days, 140°F, Dry	164	176	185
5. Exposed, 10 Days, 140°F, 100%RH	No Rxn ⁽¹⁾	No Rxn	No Rxn

(1) No exotherm reaction detected

6.6 Recommended Acceptance Criteria for FM400 Adhesive

Table 25 lists the physiochemical tests and limits recommended for receiving quality control for FM400 adhesive. Test method development, and multiple batch testing to establish acceptance limits was carried out in a joint program with American Cyanamid's Stamford Research Laboratories. The analysis, Para. 6.1, was carried out independently at MCAIR.

TABLE 25

PHYSIOCHEMICAL QUALITY CONTROL OF FM400 ADHESIVE

Properties of Uncured Adhesive	Requirements (Per Methods in Appendix)
Curing Agent (Wt.%)	2.90 - 4.21
Epoxide Ratio	0.43 - 0.53
Water (Wt.%)	0.3 Max.
DSC (Exotherm Peak Temperature, °C at 5°C/Min.)	176 - 182
DSC (Minor Endotherm Temperature, C°)	250 - 260 ⁽¹⁾

(1) If minor endotherm is not detected within this temperature range, perform a separate IR identification analysis on a separated piece of supporting scrim. Improper scrim is grounds for rejection.

7. AMERICAN CYANAMID BR400 PRIMER

7.1 Analysis for BR400 Primer

The quantitative analysis of BR400 is given in Table 26.

TABLE 26
ANALYSIS OF BR400 PRIMER

<u>Component</u>	<u>Analysis</u>	
	<u>Parts/100 Resin</u> <u>(phr)</u>	<u>Percent</u> <u>(Wt.)</u>
Solvent	-	77.6
Corrosion Inhibitor	10	1.8
Epoxide	100	18.8
Dicyandiamide (DICY)	10	1.8

7.2 Identification and Quantitative Determinations for BR400 Components

The schematic for BR400 separation and component analysis is given in Figure 21.

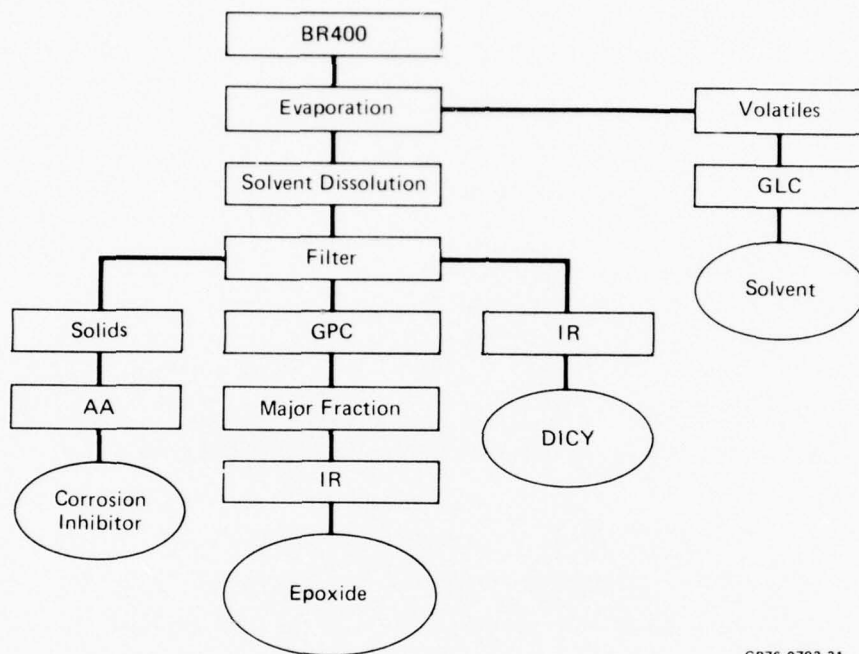
The solvent was identified by gas-liquid chromatography. The percent insoluble was determined gravimetrically and identified by quantitative atomic absorption. The curing agent, dicyandiamide, was identified and then quantitatively determined by the infrared technique. The epoxy resin was identified by IR.

7.3 Testing of Production Batches of BR400

Previous in-house testing directed toward establishing chemical acceptance criteria for BR400 included percent total solids by loss on drying. The total solids were solvent dissolved, the solution filtered and the solids ignited to determine percent corrosion inhibitor. The filtrate was diluted to volume and the percent DICY curing agent and epoxide ratio determined by quantitative IR methods given in the Appendix. Limits for the acceptance test were established from data obtained from testing five production batches, given in Table 27.

7.4 Recommended Acceptance Criteria for BR400 Primer

Table 28 lists the physiochemical tests and limits recommended for receiving quality control for BR400 primer. Test method development and multiple batch testing to establish acceptance limits was carried out in a joint program with American Cyanamid's Stamford Research Laboratories. The analysis, Para. 7.1, was carried out independently at MCAIR.



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FIGURE 21
SEPARATION AND IDENTIFICATION OF BR400 COMPONENTS

TABLE 27

CHEMICAL CONTROL TESTS FOR BR400 PRODUCTION BATCHES

<u>BATCH NO.</u>	<u>PERCENT TOTAL SOLIDS (Wt.)</u>	<u>PERCENT DICY (Wt.)</u>	<u>PERCENT INHIBITOR (Wt.)</u>	<u>EPOXIDE RATIO</u>
B-32	22.22	8.49	9.46	0.943
B-33	21.86	8.21	7.81	0.934
B-34	21.19	8.47	8.61	0.927
B-35	22.15	8.10	7.74	0.950
B-36	<u>21.01</u>	<u>8.64</u>	<u>8.32</u>	<u>0.910</u>
Average	21.69	8.38	8.39	0.933
Standard Dev.	⁺ -0.56	⁺ -0.22	⁺ -0.70	⁺ -0.015

TABLE 28

PHYSIOCHEMICAL QUALITY CONTROL OF BR400 PRIMER

<u>Properties of Uncured Primer</u>	<u>Requirements (Per Methods in Appendix)</u>
Total Solids (Wt.%)	19.5 ~ 24.5
Curing Agent (Wt.% of Total Solids)	6.0 ~ 11.0
Corrosion Inhibitor (Wt.% of Total Solids)	6.0 ~ 11.0
Epoxide Ratio	0.81 ~ 1.06

8. CONCLUSIONS AND RECOMMENDATIONS

Work accomplished during this program has demonstrated that control of the chemical formulation and condition (degree of B-staging) of 350°F curing epoxy composite prepregs and adhesives is feasible.

Analytical capabilities have been established to separate, identify and quantitatively analyze these materials as a prerequisite to establishing practical batch-to-batch chemical uniformity control methods and acceptance criteria. Thermal analysis has been shown to be a valuable quality control tool applicable to the thermosetting resin systems and to provide information relating to chemical integrity and processability.

Specific recommendations relevant to the work accomplished during this program and to the direction of future effort are as follows:

1. Improve methods of separation, identification and control of minor resin system additives. In particular, minor amounts of EPN and ECN-type novolac resins are difficult to identify and effectively control.
2. Develop a quantitative instrumental test method that is specific for CIBA MY720. This major component of many of the current systems is readily identified by GPC separation and IR spectroscopy, however, quantitative IR analysis is difficult due to solvent interference. Presently indirect control is obtained through the overall determination of WPE and epoxide ratio.
3. Improve the control methods for determining resin advancement (degree of B-staging) that occurs during subcomponent and final processing of the resin systems by the vendor. DSC methods show definite promise; however, other methods such as GPC, LLC, work in the near infrared and rheology of the resin melt should be investigated.
4. Establish the effects of variations in resin chemistry on mechanical properties, processability and moisture sensitivity.

9. REFERENCES

1. Poranski, C.F. and Moniz, W.B., "High Performance Composites and Adhesives for V/STOL Aircraft, Chemical Characterization Task", NRL Memorandum Report 3223, February 1976
2. May, C.A. "Exploratory Development for Chemical Quality Assurance and Composition of Epoxy Formulations", United States Air Force Contract No. F33615-76-C-5136, Final Report for Period 15 April 1975 to 14 April 1976.
3. Kline, Analytical Chemistry of Polymers, 12, Part 1, Interscience Publ., 1959
4. Carpenter, J.F., "Instrumental Techniques for Developing Epoxy Cure Cycles," presented at the 21st National SAMPE Symposium and Exhibition at Los Angeles, California, 6-8 April 1976.

APPENDIX A

TEST METHODS FOR CHEMICAL ANALYSIS AND CHARACTERIZATION OF EPOXY RESIN SYSTEMS

The details of the physiochemical test methods used in this program are presented.

A.1 IR Quantitative Method for CIBA Eporal, Diaminodiphenyl Sulfone (DDS)

The method for determining the diaminodiphenyl sulfone (DDS) curing agent in T300/5208 and AS/3501-6 graphite/epoxy prepregs is as follows:

- (1) Working curve procedure: Weigh (to the nearest 0.1 milligram) 50, 100, 150, and 200 milligram samples of 4, 4, diaminodiphenyl sulfone (DDS). Transfer the samples to 100ml volumetric flasks and dilute to volume with chloroform.
- (2) Place two 1.0 mm KBr precision path length, matched liquid cells filled with chloroform in both the sample and reference beams of the infrared spectrophotometer. Scan the region from 1000 to 1200 cm^{-1} to insure that no solvent absorptions appear in this region.
- (3) Replace the chloroform in the sample cell with the 50 milligram standard sample solution. For best results, the cell should be emptied and then flushed with 2-3 fresh portions of the solutions to be analyzed. Record the spectrum from 1000 to 1200 cm^{-1} . For the Beckman IR-9 infrared spectrophotometer, the following instrumental parameters are suggested:

Scan Range	1000 - 1200 cm^{-1}
Scan Speed	40 $\text{cm}^{-1}/\text{min}$
Slit	Routine (2 times std.)
Gain	3%
Period	2
Scale	0-100% T
Reference	Chloroform

Repeat the analysis for the 100, 150 and 200 milligram standards.

- (4) Sample analysis for DDS: Transfer between 1.4 and 1.6 grams of prepreg to approximately 75 milliliters of chloroform. The weight of the sample shall be measured to the nearest 0.1 milligram. Thoroughly agitate the solution to assure resin dissolution. This can be achieved by placing the solution in an ultrasonic bath for 15 minutes. Dilute the solution to 100 milliliters with chloroform and shake to assure adequate mixing.

- (5) Analyze the liquid portion of the sample in a manner identical to Step 3.
- (6) Working Curve Construction: The DDS exhibits an absorption maximum at 1110 cm^{-1} . The total absorbance of this band is calculated as follows:
Construct a baseline by connecting the minima on either side of the very sharp 1110 cm^{-1} absorbance. The total absorbance is the maximum absorbance at 1110 cm^{-1} minus the absorbance of a point which bisects the baseline and corresponds to the 1110 cm^{-1} frequency point, Figure A-1. A working curve for determining the amount of DDS in actual samples of prepreg is constructed graphically by plotting the absorbance values for the standard DDS solutions versus concentrations in mg./100 ml on linear graph paper and connecting the points with a straight line. The absorbance values should be on the ordinate (y-axis) and the amount of curing agent should be on the abscissa (x-axis), Figure A-1.
- (7) DDS Calculation: Take the absorbance value of the samples and determine the amount of DDS in the 100 ml sample by drawing a line parallel to the x-axis from the absorbance value to the straight line working curve and dropping a perpendicular line to the mg DDS/100 ml chloroform. Record the value as mg DDS/100 ml in chloroform.
- (8) Filter the remainder of the solution from Step 5 through a preweighed fritted glass crucible, retaining the graphite. Wash the graphite with copious amounts of acetone followed by drying at 100°C to constant weight. Determine the amount of graphite by subtracting the crucible weight from the graphite plus crucible weight.
- (9) The percent by weight DDS in the resin is calculated as follows:

$$\% \text{DDS} = \frac{\text{mg DDS/100 ml in Chloroform}}{\text{Sample Wt. (mg)} - \text{Graphite Wt. (mg)}} \times 100$$

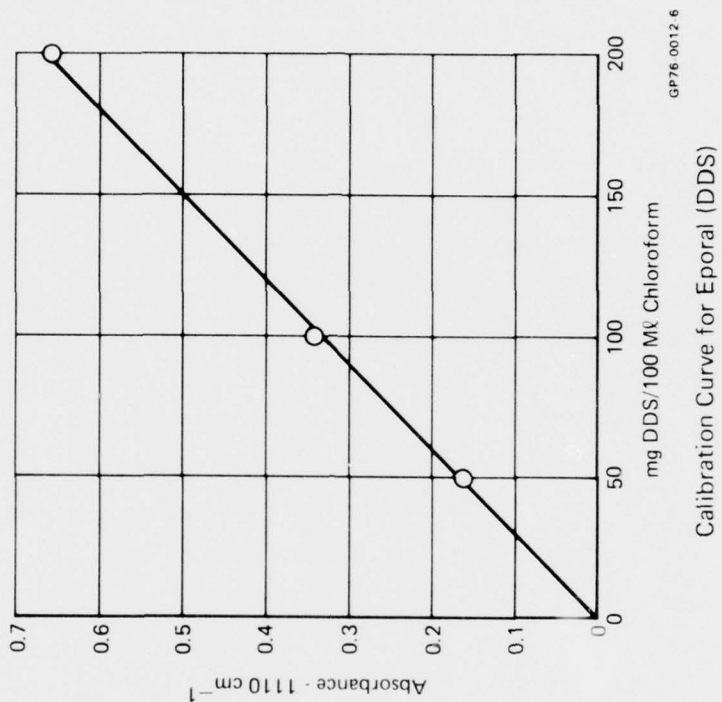
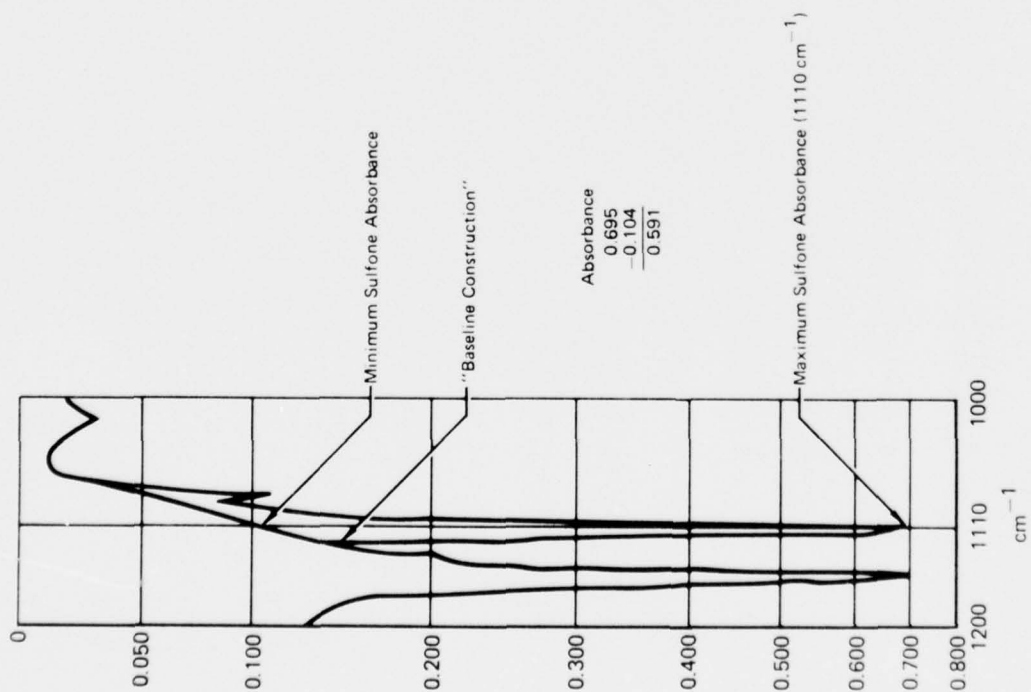


FIGURE A-1
DETERMINATION OF EPORAL (DDS) CONCENTRATION

A.2 IR Quantitative Method for Epoxide Concentration

- (1) Working curve procedure: Weigh (to the nearest 0.1 milligram) 0.5, 1.0 and 2.0 gram samples of a standard epoxide resin, of known epoxide equivalent. Transfer the samples to 50 ml. volumetric flasks and dilute to volume with N, N Dimethylformamide (DMF).
- (2) Place two 0.2 mm KBr precision path length matched liquid cells filled with DMF in both the sample and reference beams of the infrared spectrophotometer. Scan the region from 800 to 1000 cm^{-1} to insure that no solvent absorptions appear in this region.
- (3) Replace the DMF in the sample cell with the 0.5 gram standard sample solution. For best results the cell should be emptied and then flushed with 2-3 fresh portions of the solutions to be analyzed. Record the spectrum from 800 to 1000 cm^{-1} . For the Beckman IR-9 infrared spectrophotometer, the following instrumental parameters are suggested:

Scan range	800-1000 cm^{-1}
Scan speed	40 $\text{cm}^{-1}/\text{min}$
Slit	Routine (2 times std.)
Gain	3%
Period	2
Scale	0-100% T
Reference	DMF

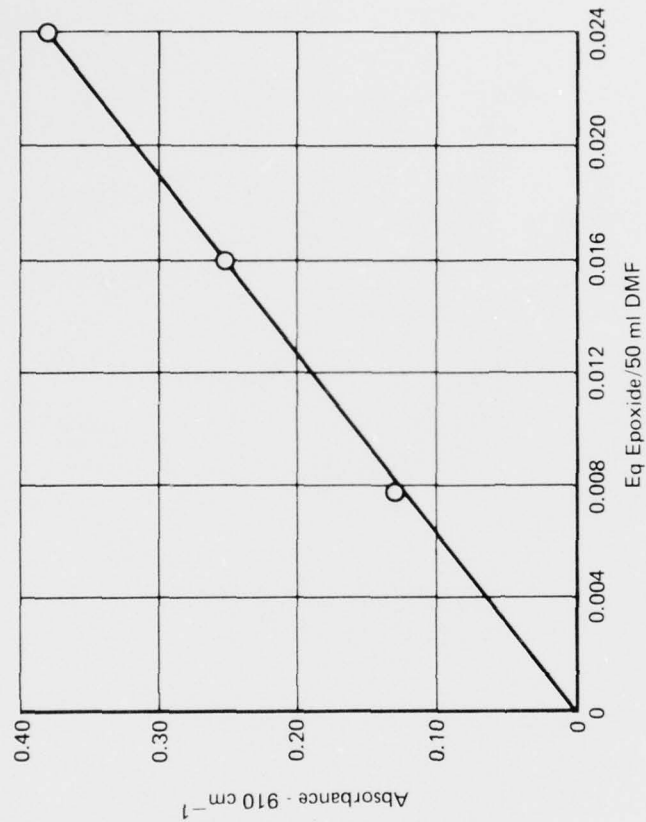
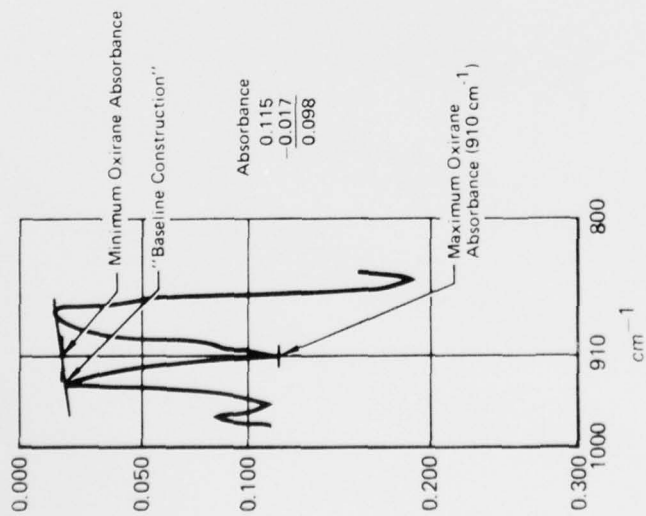
Repeat the analysis for the 1.0 and 2.0 gram standards.

- (4) Sample analysis for eq. epoxide/100 g.: Transfer between 3.3 and 4.0 grams of prepreg to approximately 35 milliliter of DMF. The weight of the sample shall be measured to the nearest 0.1 milligram. Thoroughly agitate the solution to assure resin dissolution. This can be achieved by placing the solution in an ultrasonic bath for 15 minutes. Dilute the solution to 50 milliliters with DMF and shake to assure adequate mixing.
- (5) Analyze the liquid portion of the sample in a manner identical to that described in Step 3.
- (6) Working curve construction: The oxirane group exhibits an absorption minimum at 910 cm^{-1} . The total absorbance of this band is calculated as follows:
Construct a baseline by connecting the minima on either side of the 910 cm^{-1} absorbance. The total absorbance is the maximum absorbance at 910 cm^{-1} minus

the absorbance of a point which bisects the baseline and corresponds to the 910 cm^{-1} frequency point, Figure (A-2). A working curve for determining the eq. epoxide/50 ml in actual samples of the prepreg is constructed graphically by plotting the absorbance values for the standard epoxide solutions versus concentrations in eq. epoxide/50 ml on linear graph paper, and connecting the points with a straight line. The absorbance values should be on the ordinate (y-axis) and the amount of eq. epoxide/50 ml DMF should be on the abscissa (x-axis), Figure A-2).

- (7) Eq. Epoxide/100 g Calculation: Take the absorbance value of the samples and determine the eq. epoxide in the 50 ml sample by drawing a line parallel to the x-axis from the absorbance value to the straight line working curve and dropping a perpendicular line to the eq. epoxide/50 ml DMF. Record the value as eq. epoxide/50 ml DMF.
- (8) Filter the remainder of the graphite/resin/DMF solution from Step (5) through a preweighed fritted glass crucible, retaining the graphite. Wash the graphite with copious amount of acetone followed by drying at 100°C to constant weight. Determine the amount of graphite by subtracting the crucible weight from the graphite plus crucible weight.
- (9) The eq. epoxide/100 g of resin is calculated as follows:

$$\text{Equivalent Epoxide/100 g Resin} = \frac{\text{Eq. Epoxide/50 ml DMF}}{\text{Sample Wt.} - \text{Graphite Wt.}} \times 100$$



IR Measurement of Oxirane Absorbance

Calibration Curve for Standard Epoxide

FIGURE A-2
DETERMINATION OF EPOXIDE CONCENTRATION

A.3 Liquid-Liquid Chromatographic Method for Epoxide No.2N Concentration (5208 Resin)

- (1) Equipment and operating conditions: Use a Waters Associates ALC/GPC 301 Analytical Liquid Chromatograph or equivalent fitted with a Schoeffel SF770 Spectroflow-monitor variable wavelength UV detector for monitoring the column effluent. The ultraviolet (UV) spectrum of Epoxide No.2N shows a maximum absorbance at a wave length of 280 nanometers (nm) rather than the 254 nm range at which most liquid chromatographic (LC) ultraviolet detectors are operated. Accurate quantitative determination of Epoxide No.2N requires a variable wave length UV detector that can be repeatedly set at 280 nm.
Operate the chromatographic column system in the reverse-phase liquid-liquid chromatographic (RV-LLC) mode using a 30 cm x 4 mm I.D. column packed with μ Bondapak C₁₈ material from Waters. The μ Bondapak C₁₈ packing is relatively non-polar and is effective for separating resins based on functionality rather than on molecular size. Use 30 volume percent tetrahydrofuron (THF) plus 70 volume percent water as the elution solvent. Maintain the flow-rate of the elution solvent through the column at 0.8 ml/minute.
- (2) Prepare the Epoxide No.2N and 5208 resin systems to be analyzed in the THF solutions at a concentration of 40 milligrams of resin/ml of THF. Inject 5 microliters of the THF solutions into the chromatograph for determination of the amount of Epoxide No.2N in 5208. Epoxide No.2N has an elution volume between 48-56 ml under the above operating conditions. As shown in Figure A-3, the bulk of the peaks in the RV-LLC chromatogram of 5208 are from the Epoxide No.1N epoxy resin component of 5208; however, no peaks from Epoxide No.1N interfere with the peak for Epoxide No.2N.
- (3) Determine the amount of Epoxide No.2N in the 5208, using both internal standard and external standard techniques. For the internal standard technique, analyze a 5208 sample under the above conditions and determine the peak area for Epoxide No.2N in the unknown material by triangulation (peak height x peak width at half-height). Add a known amount of Epoxide No.2N to the same 5208 solution and repeat the analysis. Calculate the weight of Epoxide No.2N in the 5208 sample from the following expression:

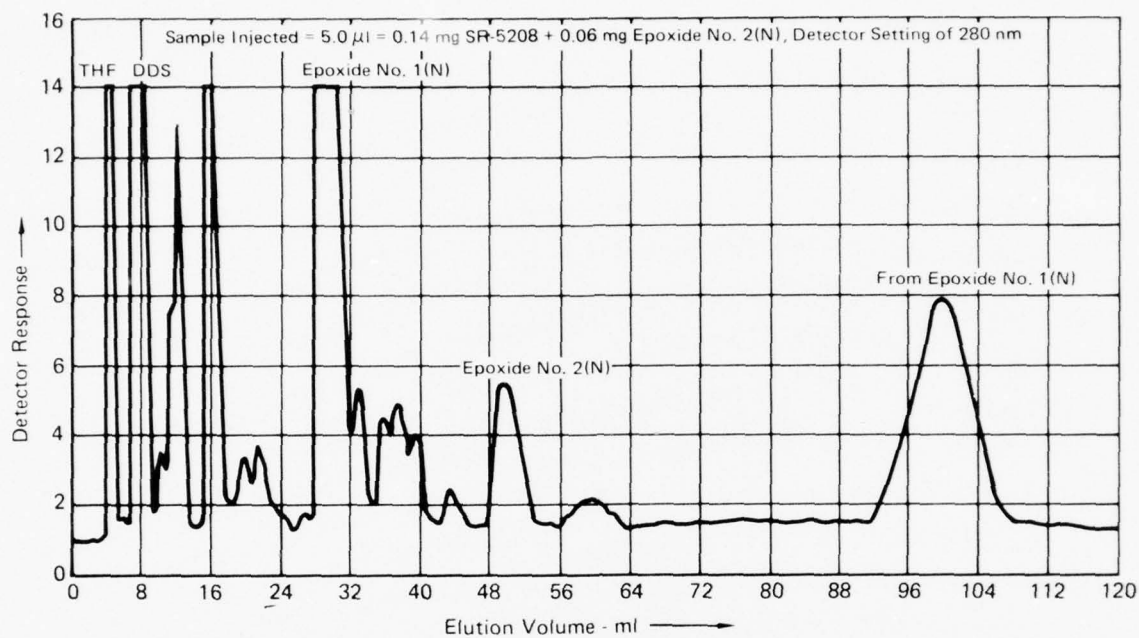


FIGURE A-3
CHROMATOGRAM OF SR-5208 + 25.8% WT EPOXIDE NO. 2 (N)

$$W_u = \frac{(W_s) (PA_u)}{(PA_t - PA_u)}$$

where: W_u = weight Epoxide No.2N in 5208 sample being analyzed.

W_s = weight of Epoxide No.2N added to the 5208 solution.

PA_u = peak area for Epoxide No.2N in 5208 sample being analyzed.

PA_t = total peak area for Epoxide No.2N in 5208 sample plus the added Epoxide No.2N.

$PA_t - PA_u$ = peak area for added amount of Epoxide No.2N.

For the external standard technique, prepare calibration solutions of different concentration of Epoxide No.2N in THF. Analyze the calibration solutions and the calculate peak areas in the usual manner. Prepare an absolute calibration curve of peak area vs. the weight of Epoxide No.2N in the calibration solutions. Determine the weight of Epoxide No.2N in an unknown 5208 batch directly from the curve. The percent weight of Epoxide No.2N reported is the average of the results obtained using both the internal and external standard techniques.

- (4) The analysis is performed on the T300/5208 prepreg. Make up the solutions as described, filter and quantitatively determine the graphite fiber weight in the sample. Calculate the weight percent Epoxide No.2N in the resin.

A.4 Thermal Analysis of Resin Systems Using Differential Scanning Calorimetry (DSC)

- (1) Use the DuPont 990 Thermal Analysis System or the equivalent Perkin-Elmer or Mettler equipment in the DSC mode.
- (2) Generate DSC thermograms in static air using 10-15 mg of prepreg or adhesive. Satisfactory sensitivity for the DuPont 990 is obtained using settings of 0.1 to 1.0 mcal/sec/in and a scale setting of 50°C/inch chart speed.
- (3) Determine the exotherm peak temperatures for a series of three DSC runs at different heating rates, e.g. 2, 5 and 10°C/min. Reduce the data by obtaining the best straight line fit by linear regression of the Arrhenius expression:

$$\log \emptyset = A/T + B$$

Where:

\emptyset = Heating rate (°C/Min)

T = Temperature (°K)

A = Constant, related to activation energy

B = Constant, related to the Arrhenius frequency factor

Statistical fit should exceed $r^2 = 0.98$. If not, repeat runs as necessary to improve statistical fit.

- (4) Report the exotherm peak temperature in °C for a progression of 5°C/min calculated from the best straight line formula from Step (3).

A.5 Atomic Absorption Method for Boron Trifluoride Catalyst

- (1) Use a Perkin Elmer 503 or equivalent atomic absorption spectrophotometer. The amount of boron trifluoride organo complex is determined by measuring the atomic absorption of boron. For the 503 instrument, set up to obtain maximum absorbance with an aqueous solution of boron in a nitrous oxide - acetylene flame, the parameters are as follows:

Wavelength	:	249.7 nm
Slit Setting	:	0.7 nm (-4)
Light Source	:	Boron hollow cathode lamp
Nitrous Oxide Flow	:	40
Acetylene Flow	:	70
Integration Period	:	10 seconds

Note: Flow meter settings will change when sample is introduced and must be adjusted to obtain maximum sensitivity.

- (2) Prepare a working curve by measuring the absorbance of boron for at least three standards that are prepared by weighing known amounts of the organo complex (e.g. boron trifluoride monoethylamine), dissolving and diluting to known volumes in methyl isobutyl ketone (MIBK). The standards should contain amounts of the complex at less than, approximately equal to and greater than the amount contained in the sample. The data for a typical working curve useful in the range of boron complex present in preregs, i.e. 1%, is as follows:

<u>Grams Complex</u>	<u>Final Volume (ml)</u>	<u>Absorbance</u>
0.0600	100	0.011
0.1307	100	0.025
0.2021	100	0.037

- (3) Prepare the prepreg sample by transferring about eight (8) grams of prepreg to approximately 75 ml of MIBK (weigh to nearest 0.1 mg). Thoroughly agitate the solution in an ultrasonic bath for 15 minutes to assure dissolution. Dilute the solution to 100 ml with MIBK and shake thoroughly. Withdraw a sample for examination by atomic absorption. Filter the remainder onto a weighed fritted filter. Determine the weight of graphite. Use the working curve to calculate the weight percent boron complex in the resin as follows:

$$\% \text{ BF}_3 \text{ complex} = \frac{\text{g/100 ml} \times 100}{\text{wt. of sample} - \text{wt. of graphite}}$$

A.6 IR Quantitative Method for Epoxide No.2H (3501-6 Resin)

- (1) Working Curve Procedure: Weigh (to the nearest 0.1 milligram) 50, 100, 150, and 200 milligram samples of Epoxide No.2H. Transfer the samples to 100 ml volumetric flasks and dilute to volume with chloroform.
- (2) Place two 1.0 mm KBr precision path length matched liquid cells filled with chloroform in both the sample and reference beams of the infrared spectrophotometer. Scan the region from 1600 to 1800 cm^{-1} to insure that no solvent absorptions appear in this region.
- (3) Replace the chloroform in the sample cell with the 50 milligram standard sample solution. For best results the cell should be emptied and then flushed with 2-3 fresh portions of the solution to be analyzed. Record the spectrum from 1600 to 1800 cm^{-1} . If recording the spectrum with a Beckman IR-9 infrared spectrophotometer, the following instrumental parameters are suggested:

Scan range	1600-1800 cm^{-1}
Scan speed	40 $\text{cm}^{-1}/\text{min}$
Slit	Routine (2 times std)
Gain	3%
Period	2
Scale	0 - 100% T
Reference	Chloroform

Repeat the analysis for the 100, 150, and 200 milligram standards.

- (4) Sample analysis for Epoxide No.2H: Transfer between 2.5 and 3.0 grams of prepreg to approximately 75 milliliters of chloroform. (Weigh to the nearest 0.1 milligram.) Thoroughly agitate the solution to assure resin dissolution. This can be achieved by placing the solution in an ultrasonic bath for 15 minutes. Dilute the solution to 100 milliliters with chloroform and shake to assure adequate mixing.
- (5) Analyze the liquid portion of the sample in a manner identical to that described in step (3). Filter off the graphite fibers and obtain weight.
- (6) Working Curve Construction: The Epoxide No.2H exhibits an absorption maximum at 1730 cm^{-1} . The total absorbance of this band is calculated as follows: Construct a baseline by connecting the minima on either side of the 1730 cm^{-1} minus the absorbance of a point which bisects

the baseline and corresponds to the 1730 cm^{-1} frequency point. A working curve for determining the amount of Epoxide No.2H in actual samples of the prepreg is constructed graphically as follows. Plot the absorbance value for the standard Epoxide No.2H solutions versus concentration in mg/100 ml on linear graph paper and connect the points with a straight line. The absorbance values should be on the ordinate (y-axis) and the amount of Epoxide No.2H/100 ml should be on the abscissa (x-axis).

- (7) Epoxide No.2H calculations: Take the absorbance value of the samples and determine the amount of Epoxide No.2H in the 100 ml sample as follows: Draw a line parallel to the x-axis from the absorbance value to the straight line working curve. Drop a perpendicular line to the Epoxide No.2H/100 ml chloroform and record. The weight percent Epoxide No.2H in the resin is calculated as follows:

$$\% \text{ Epoxide No.2H} = \frac{\text{mg Epoxide No. 2/100 ml in chloroform}}{\text{sample wt (mg) - graphite wt. (mg)}} \times 100$$

A.7 Gas-Liquid Chromatographic Method for Epoxide No.2H and Epoxide No.3H (3501-6 Resin)

- (1) Use a Hewlett-Packard Model 5750 gas-liquid chromatographic (GLC) unit or equivalent equipped with a flame ionization detector and using Dexsil 300 columns. Dexsil 300 is a polycarboranesiloxane material with high thermal stability that can be operated between 50-500°C and can be maintained for sustained periods above 400°C without loss of separation efficiency.
- (2) The weight percent of unreacted or "free" Epoxide No.3H in 3501-6 is determined by the comparison of peak heights for standard solutions of Epoxide No.3H with peak heights obtained for Epoxide No.3H in unknown sample solutions of 3501-6. Prepare the standard solutions by dissolving 0.5 grams and 1.0 gram of Epoxide No.3H in 25 ml portions of acetone and prepare the unknown sample solution by dissolving 1.0 gram of 3501-6 in 25 ml of acetone. The operating conditions for the GLC are as follows:

Initial Column Temperature	: 175°C
Final Column Temperature	: 300°C (Hold till analysis complete)
Column Temperature Rise Rate	: 15°C/minute
Vaporizer Temperature	: 280°C
Detector Temperature	: 250°C
Electrometer Current Range	: 8×10^{-9} amperes
Sample Sizes	: 2.0 μ l for the Epoxide No. 3 standard solutions and 5.0 μ l of the unknown 3501-6 solution

Under the above operating conditions, the two major peaks indicative of Epoxide No.3H elute at 8.6 and 9.5 minutes.

- (3) The weight percent of unreacted or "free" Epoxide No.2H in 3501-6 is determined by the comparison of peak heights for standard solutions of Epoxide No.2H with peak heights obtained for Epoxide No.2H in unknown sample solutions of 3501-6. Prepare the standard solutions by dissolving 0.5 grams and 1.0 gram of Epoxide No.2H in 25 ml portions of acetone and prepare the unknown sample solution by again dissolving 1.0 gram of 3501-6 in 25 ml of acetone. For this quantitative analysis of Epoxide No.2H in 3501-6, the GLC system incorporating the Dexsil 300 columns is operated under the same conditions as for the determination of the Epoxide No.3H. Using these operating conditions, the two major peaks indicative of Epoxide No.2H elute at 4.8 and 5.0 minutes.

- (4) Chromatograms used for the analysis are similar to those shown for the original identification of Epoxide No.2H and Epoxide No.3H, Figures A-4 and A-5.

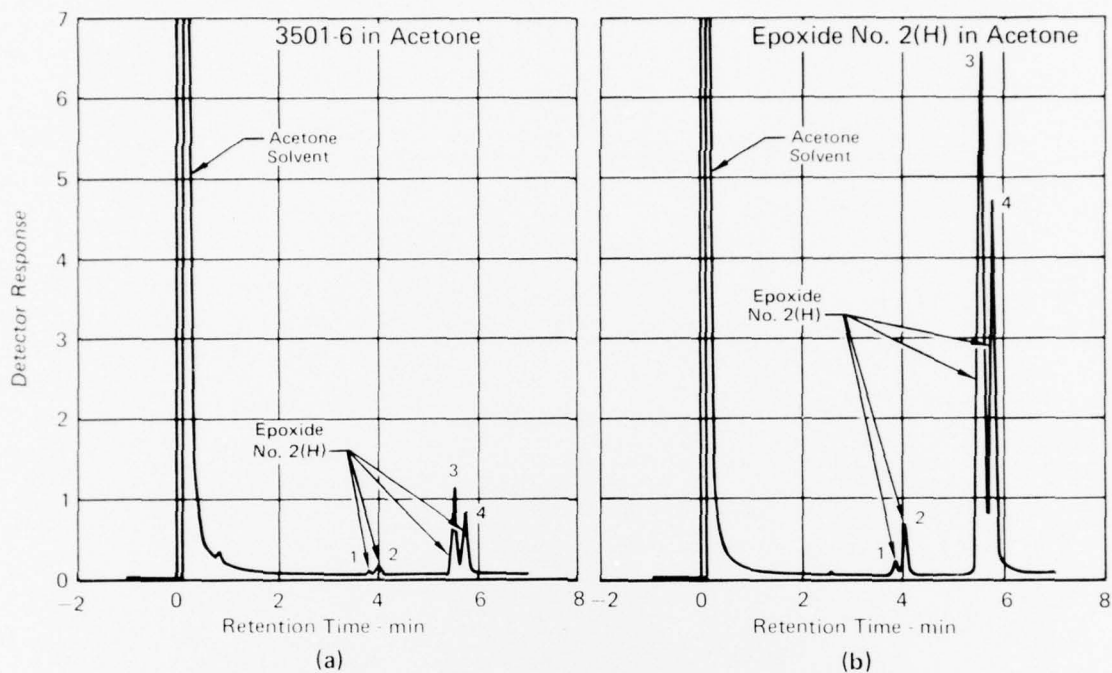


FIGURE A-4
IDENTIFICATION OF EPOXIDE NO. 2(H) IN 3501-6 RESIN
BY GAS PHASE CHROMATOGRAPHY

GP76 0283 2

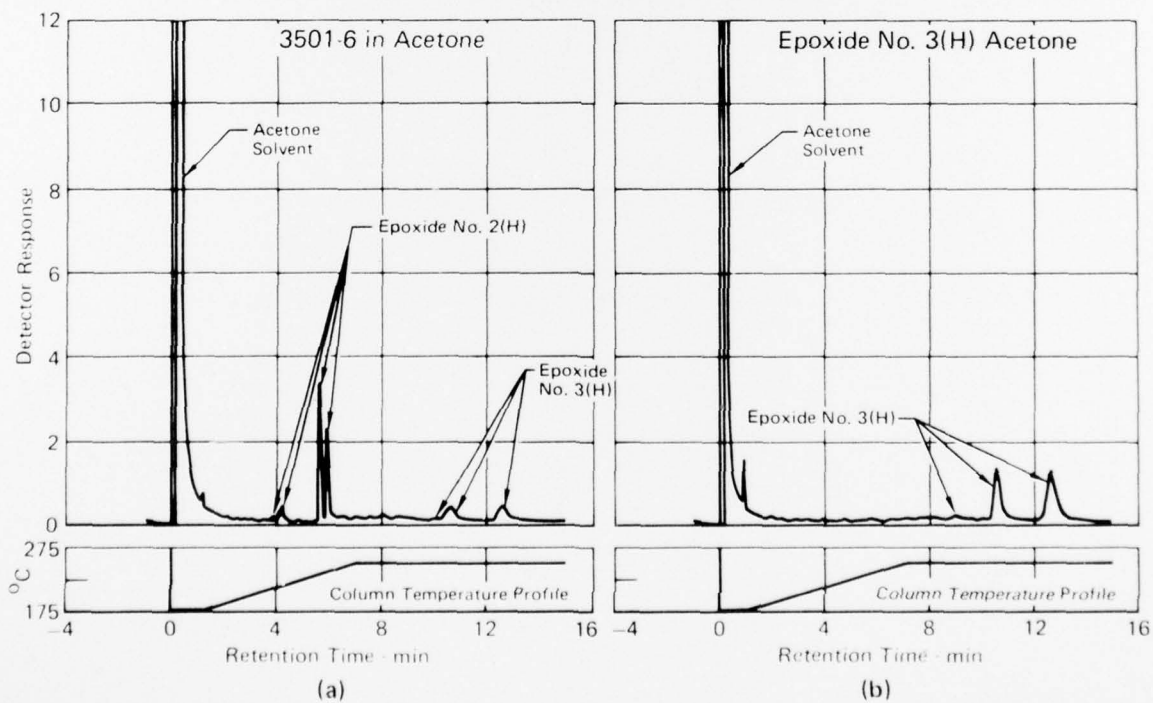


FIGURE A-5
IDENTIFICATION OF EPOXIDE NO. 3(H) IN 3501-6 RESIN
BY GAS PHASE CHROMATOGRAPHY

GP76 0283 7

A.8 IR Quantitative Method for Epoxide Ratio (FM400)

- (1) Remove the cover backing from a four square inch piece of adhesive tape and place in a 150 ml beaker. Add approximately 50 ml of 99 mole % acetone and agitate the solution until the filler (e.g., metal powder) readily separates from the scrim cloth. Transfer the contents of the beaker to a fluted filter and remove all solids from solution. Evaporate the acetone under vacuum at ambient temperature for 12-24 hours. Place a small amount of the viscous resin system on a KBr salt plate and prepare a thin uniform film suitable for infrared measurements.
- (2) Place the sample in a Beckman IR9 or equivalent spectrophotometer with the salt plate placed at zero degree orientation, and record the infrared spectrum using the following instrumental parameters:

Scan Range $750-950\text{ cm}^{-1}$

Scan Speed $80\text{ cm}^{-1}/\text{min}$

Gain 3%

Period 2

Slit Routine (2 times standard)

Scale 0-100% T

Reference Air

The total maximum absorbance for the 800 cm^{-1} internal standard band should be in the 0.3 to 0.6 range.

- (3) Determine the internal standard band at 800 cm^{-1} as follows: Construct a baseline by drawing a straight line between the minima at 705 cm^{-1} and 875 cm^{-1} . The total absorbance is then the maximum absorbance of the 800 cm^{-1} frequency point. For example, if the maximum absorbance is 0.480 and the minimum baseline absorbance is 0.060, the total absorbance is $0.480 - 0.060 = 0.420$.
- (4) The absorbance of 910 cm^{-1} epoxide band is calculated as follows: Construct a baseline by drawing a straight line between the minima at 875 cm^{-1} and 925 cm^{-1} . The total absorbance is the maximum absorbance of the 910 cm^{-1} minus the absorbance reading at a point which passes through the baseline and corresponds to the 910 cm^{-1} frequency point. For example, if the maximum absorbance is 0.305 and the minimum baseline absorbance is 0.105, the total absorbance is $0.305 - 0.105 = 0.200$.

- (5) The calculation of an epoxide ratio is a measure of oxirane functionality. The epoxide ratio is calculated by dividing the total absorbance of the 800 cm^{-1} band into the total absorbance of the 910 cm^{-1} oxirane band.

For example, if the 800 cm^{-1} absorbance is 0.420 and the 910 cm^{-1} absorbance is 0.215, the epoxide ratio is $0.215/0.420 = 0.512$.

The absorbance bands and their measurement for obtaining the epoxide ratio are illustrated in Figure A-6.

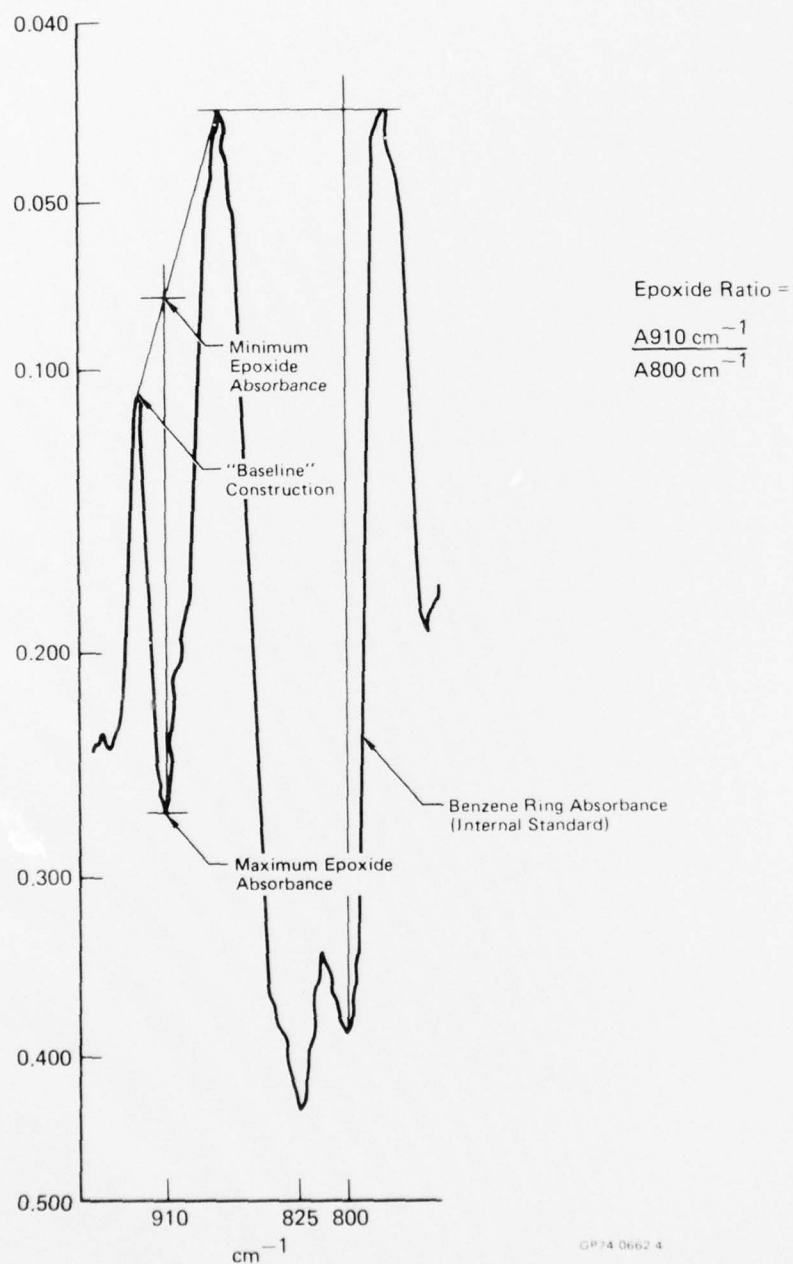


FIGURE A-6
IR DETERMINATION OF EPOXIDE RATIO

A.9 IR Quantitative Method for Dicyandiamide (DICY)

(1) Working Curve Procedure: Weigh (to the nearest 0.1 milligram) 10, 20, 30, 40 and 50 milligram samples of reagent grade dicyandiamide. The DICY should be predried for 2 hours at 110°C and allowed to cool in a dessicator. Transfer the samples to 100 ml volumetric flasks and dilute to volume with 99 mole % acetone.

(2) Place two 1.0 mm KBr stainless steel precision pathlength matched liquid cells filled with 99 mole % acetone in both the sample and reference beams of the Beckman IR9 infrared spectrophotometer or equivalent instrument. Scan the region from 2000 to 2300 cm^{-1} to insure that no solvent absorptions appear in this region. Replace the acetone in the sample cell with the 10 mg. sample solution. For accurate results, the cell should be emptied and then flushed with 2-3 fresh portions of the solution to be analyzed. Record the spectrum using the following instrumental parameters for the Beckman IR-9 infrared spectrophotometer:

Scan Range	2000-2300 cm^{-1}
Scan Speed	40 $\text{cm}^{-1}/\text{min}$
Slit	Routine (2 times standard)
Gain	3%
Period	2
Scale	0-100% T
Reference	99 mole % acetone

Make two independent measurements on the sample.

Repeat the analysis for the 20, 30, 40, and 50 milligram samples.

The sample cell should be flushed with fresh 99 mole % acetone as well as the solution to be measured.

(3) Remove both the cover and backing from two separate pieces of adhesive. Transfer these samples to two tared 150 ml beakers and weigh to the nearest 0.1 mg. The sample weights shall be between 1.40 and 1.70 grams.

Add approximately 60 ml of 99 mole % acetone and swirl the beakers until the filler readily separates from the scrim cloth. Remove the scrim cloth with tweezers and transfer to a tared 100-150 ml beaker. Rinse the scrim cloth with a small amount of fresh acetone and insure that the rinse is added to the beaker. Dry the scrim cloth at room

temperature and weigh. Calculate the weight of the scrim cloth (carrier) to 0.1 mg.

Transfer the solutions quantitatively to a high speed centrifuge and remove the solids. Wash the solids several times with fresh acetone to insure quantitative separation. Transfer the centrifugate solutions quantitatively to two 100 ml volumetric flasks and dilute to volume. Analyze the samples in a manner identical to the procedure used in preparing the working curve.

- (4) Working Curve Construction: The nitrile band of dicyandiamide exhibits an absorption maximum at 2190 cm^{-1} . The total absorbance of this band is calculated as follows: Construct a baseline by connecting the minima on either side of the very sharp 2190 cm^{-1} absorbance. The total absorbance is the maximum absorbance at 2190 cm^{-1} minus the absorbance of a point which bisects the baseline and corresponds to the 2190 cm^{-1} frequency point.

A working curve for determining the amount of curing agent in actual samples of FM400 is constructed graphically as follows: Average the absorbance values for each of the two runs of the 10, 20, 30, 40, and 50 mg. samples. Plot this average absorbance value versus concentration in mg/100 ml on linear graph paper, and connect the points with a straight line. The absorbance values should be on the ordinate (y-axis) and the amount of curing agent should be on the abscissa (x-axis). The scale shall be such that absorbance can be determined to ± 0.005 absorbance units and the amount determined to ± 0.5 mg. The y-intercept should be near zero.

- (5) Dicyandiamide Calculation: Measure the absorbance of the nitrile band. Take the average absorbance value of the two samples. Determine the amount of curing agent present in the 100 ml sample as follows: Draw a line parallel to the x-axis from the absorbance value to the straight line working curve. Drop a perpendicular line to the "mg./100 ml acetone" axis and record this value.

The percentage of the curing agent will be calculated as follows:

$$\% \text{DICY} = \frac{\text{g. curing agent/100 ml acetone}}{\text{sample wt.} - \text{carrier wt.}} \times 100$$

A.10 - Gas Chromatographic Method for Water in FM400 Adhesive

- (1) Working Curve Procedure: Weigh (to the nearest 0.1 mg.) 5, 15, 25, and 35 mg. samples of distilled water in 25 ml volumetric flasks. Dilute these standards to volume using reagent grade methylene chloride (dichloromethane) from a previously unopened pint bottle.

The instrumental parameters for the HP5750 gas chromatograph are as follows:

Column Temperature	Stable @ 135°C
Injector Temperature	125°C
Detector Temperature	115°C
Helium Flow Rate	40-60 cc/min.
Detector Bridge Current	195 milliamps
Column	5' x 1/4" stainless steel Poropak Q-S ³

Inject an 8-microliter sample of methylene chloride (from the bottle used to prepare the standards) into the HP5750 gas chromatograph equipped with a thermal conductivity (hot wire) detector. Air should be injected deliberately for use as a reference point. The water peak, if present, will elute between the small air peak and the gross solvent response. The area of the water peak obtained in this step will constitute the solvent "back-ground".

Inject an 8-microliter aliquot of the standard 5 mg./25 ml sample into the chromatograph and determine the area of the water peak. Repeat this three times for a total of four analyses on the standard.

Repeat the above paragraph for the remaining 15, 25, and 35 mg. samples.

- (2) Procedure for Water Determination: Weigh (to the nearest 0.1) a 4.0 to 5.0 gram sample of adhesive that has had the backing material removed. Place the adhesive with the protective cover in a 50 ml glass stoppered centrifuge tube. Add exactly 25.0 ml of reagent grade methylene chloride (from the bottle used for the blank and standard determination) and cover. Swirl the solution until the resin is completely dissolved. When the resin is dissolved, the filler will readily separate from the scrim carrier cloth. Centrifuge the solution to remove the filler material and effect a clear non-turbid solution.

Inject an 8-microliter sample from the solution described in the previous paragraph into the HP5750 gas chromatograph and record the area of the water peak. Repeat this for a total of four runs.

Remove the protective cover material and scrim cloth. Rinse with acetone and air dry for 20 minutes. Weigh both the cover material and scrim cloth to the nearest 0.1 mg. and sum. This weight will be subtracted from the weight obtained initially to ascertain the corrected sample weight.

- (3) Working Curve Preparation: Subtract the solvent background from each of the sixteen data points to determine the true water response.

Plot the water response on the y-axis (ordinate) versus the amount of water (mg./25 ml) on the x-axis (abscissa) using linear graph paper. Perform a least squares analysis of the data to determine the best straight line fit, and draw this line on the graph paper. The graph paper should be such that the response can be read to ± 0.1 units and the amount of water to ± 0.1 mg.

- (4) Calculation of Water Content: Subtract the solvent background response from each of the values for water determined as above and calculate the arithmetic mean of the corrected water response.

Determine the amount of water present in the 25 ml sample as follows: Draw a line parallel to the x-axis from the response value to the straight line working curve. Drop a perpendicular line to the "mg./25 ml" axis and record this value.

The percentage of water in the sample may be calculated as

$$\% \text{ Water} = \frac{\text{"g. water/25 ml"}}{\text{sample wt.} - (\text{scrim carrier wt.} + \text{cover material wt.})} \times 100$$

For example, if the sample weight were 6.3220 g, the cover material plus carrier weight 0.3017 g, and 7.3 mg. of water were found by gas chromatographic analysis, the percentage of water would be

$$\frac{0.0073}{6.3220 - 0.3017} \times 100 = 0.122\%$$

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